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CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY
EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

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OCTOBER, 1911

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THE

PHYSICAL REVIEW.

SOME THERMODYNAMIC PROPERTIES OF AIR AND OF CARBON DIOXIDE.

By A. G. Worthing.

I. Introduction.

GAY-LUSSAC[1] was the first to investigate the question as to whether or not the internal energy of a mass of gas is a function of its volume. He was not able to conclude that the internal energy was a function of the volume. On Gay-Lussac's work R. Mayer[2] based his computations for the mechanical equivalent of heat. Joule[3] with somewhat greater care and with a modified method came to the same conclusion. In each of these experiments, the gas under consideration was allowed to expand freely, that is without the performance of external work and without the addition or subtraction of heat. This latter condition was only imperfectly realized. The question as to whether or not the internal energy of the gas was a function of the volume depended directly on whether or not the freely expanding mass of gas taken as a whole suffered any change in temperature. The ratio of such a change in temperature to the change in pressure for small changes in pressure is called the free-expansion effect. Later repetitions of Joule's experiment by Regnault[5] and by Hirn[6] led to the same result. Cazin[7] about 1870 sought to do away with errors due to heating. He noted the variations with time of a fluctuating liquid pressure gauge one side of which was connected to the chamber containing the gas under experimentation. Cazin concluded that the internal energy of a gas was a function of its volume and obtained values therefor which will be noted later. Due to the use of extended extrapolations and the presence of heating effects in the stop-cock separating his two chambers initially, the results are of doubtful significance. The writer is in receipt of a letter from Professor R. A. Millikan, in which he states that he has tried a method differing

from Cazin's in that the fluctuations of the liquid in the pressure gauge were eliminated by a null method. He was not able, however, to eliminate the heating effects at the stop-cock.

The method first successfully employed was due to Joule and Thomson[9] (Lord Kelvin). Their celebrated porous plug experiments gave consistent results, which only needed corrections for external work done by the gas in the expansion in order to show the dependency of the internal energy of the gas upon the volume. The physical quantity (μ) determined by them was the ratio of the change in temperature to the change in pressure for small changes of pressures occurring as the gas passed through the porous plug. This quantity has since received the name Joule-Thomson effect or Joule-Kelvin effect. For moderate pressures they found μ independent of the pressure and dependent on the temperature as shown in (1),

$$\mu = A/\theta^2. \tag{1}$$

Rose-Innes,[10] D. Berthelot[11] and Buckingham[12] have given other equations for representing the same effect.

Natanson,[13] working with CO_2 under higher pressures, found a noticeable though small diminution in the Joule-Kelvin effect for increased pressures. Kester,[14] working with CO_2 under still greater pressures, did not find this change due to the change in pressure. Rudge[15] has recently made some rough determinations for CO_2 with a modified method, in which the gas escapes from a pierced bulb in a calorimeter, through a long piece of narrow tubing. His results as a whole are in agreement with those of the previous experiments mentioned. Recently Dalton,[16] working with air, has found an effect similar to that found by Natanson for CO_2. Witkowski,[17] having in view the applications to liquid air machines, applied thermodynamic formulæ to a great many experimentally determined results. He computed by graphical methods a series of curves which were drawn on a pressure-temperature diagram, the slopes of which at any point give directly for that point the Joule-Kelvin and the free-expansion effects. Many steps are involved in reaching the final results, and confirmation is needed for this highly important work. Searle,[8] making use of Van der Waal's equation and assuming the constancy of the isometric heat capacity, computed for CO_2 the change in temperature for the gas expanding from a pressure of 10 atmos. to 5 atmos. Some of the results of these investigations will be noted later.

The present paper is the immediate outcome of an attempt to better comprehend the dependency of the ratio of the two heat capacities of a substance γ on its pressure and temperature. It has led to the develop-

ment of a certain thermodynamical equation which relates the ratio γ to the free-expansion effect. This together with another well-known relation for the Joule-Kelvin effect has been used in computing these effects for air and CO_2. There existed what seemed to be satisfactory data for air. An experimental study of γ for CO_2 was undertaken in this connection to complete what seemed necessary data for that gas.

II. Derivation of Formulæ Relating the Ratio γ to the Free-Expansion and the Joule-Kelvin Effects.

For convenience there is given in Table I. the symbols and the units of some of the quantities used in this discussion.

Definitions of N. V. Unit, T. N. V. Unit, μ and η.—The "normal volume unit" (N. V. unit) of a substance is defined by K. Onnes[25] as the volume actually occupied at 0° C. by one gram-molecule of the substance when under a pressure of one atmosphere. The "theoretical normal volume unit" (T. N. V. unit) is defined as the volume that would

Table I.

Symbols and units of some of the quantities used.

Quantity.	Symbol.	Unit.
Pressure,	p	atmosphere.
Specific volume,	v	$\frac{\text{N. V. unit}}{\text{gr. mol.}}$, $\frac{\text{T. N. V. unit}}{\text{gr. mol.}}$.
Temperature,	T	degree Centigrade.
Thermodynamic temperature,	θ	degree Kelvin.
Time,	t	second.
Reduced pressure,	π	critical pressure.
Reduced temperature,	τ	critical temperature.
Reduced specific volume,	ν	critical specific volume.
Quantity of heat,	Q	atmo. × N. V. unit.
Specific internal energy,	ϵ	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.}}$.
Isopiestic heat capacity,	C_p	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}$, $\frac{\text{calories}}{\text{gr.} \times \text{deg.}}$.
Isometric heat capacity,	C_v	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}$, $\frac{\text{calories}}{\text{gr.} \times \text{deg.}}$.
Ratio of the two heat capacities,	γ	
Internal work in infinitesimal, reversible, isothermal expansions,	ΔW_1	atmo. × N. V. unit.
External work in infinitesimal, reversible, isothermal expansions,	ΔW_2	atmo. × N. V. unit.
Free-expansion effect,	η	$\frac{\text{deg.}}{\text{atmo.}}$.
Joule-Kelvin effect,	μ	$\frac{\text{deg.}}{\text{atmo.}}$.

be occupied at 0° C. by one gram-molecule of the substance under a pressure of 1 atmosphere if the gas obeyed Boyle's Law. It is assumed that the value of the product pv in such a case is the value of pv which may be obtained by extrapolation to zero pressure when considering the behavior of the actual gas. The measuring of volume in such units requires that C_p, C_v and ϵ be expressed in the units given in Table I. instead of the common units of cal./(gr. × deg.) and cal./gram. The free-expansion effect, η, of a substance, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance into a vacuum. Mathematically it is

$$\eta = (\partial\theta/\partial p)_\epsilon. \tag{2}$$

The Joule-Kelvin effect, μ, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance through an orifice or a porous plug from one maintained pressure to another maintained pressure. Mathematically it is

$$\mu = (\partial\theta/\partial p)_{\epsilon+pv}. \tag{3}$$

For the sake of accuracy in the theoretical discussions, it has been necessary to express temperature in the units of the thermodynamic scale. For other purposes it makes but little difference in the present work whether temperatures are measured in this scale or in the more common centigrade scale. In the adapting of experimental data, the writer has assumed that the degree Kelvin and the degree centigrade were equal.

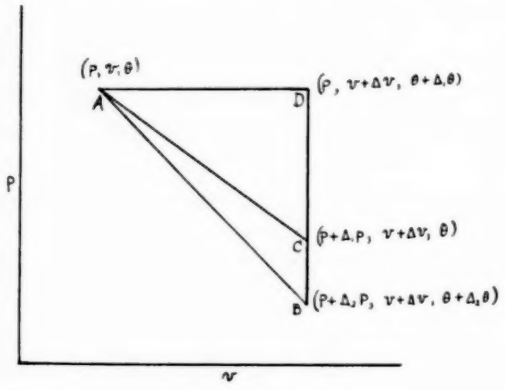

Fig. 1.

Derivation of Equation Relating η and γ. — The equation relating η, the free-expansion effect, to γ, the ratio of the two heat capacities may be readily obtained. Consider hanges in ϵ, the internal energy of the substance under consideration, for transformations indicated in Fig. 1. Let the change represented by the straight line AB be an infinitesimal transformation in which there is no change in the specific internal energy ϵ,

an infinitesimal free-expansion. Let the changes represented by AD, DB and AC be respectively infinitesimal isopiestic, isometric and isothermal transformations. Due to carrying the substance around the cycle $ABDA$, no resultant change occurs in ϵ. Consequently the individual changes in ϵ occurring in the individual transformation making up the cycle must sum up to zero. Moreover, since there are no changes in ϵ along AB, the changes in ϵ in passing along BD and DA must sum up to zero. Hence

$$C_v(\Delta_1\theta - \Delta_2\theta) - C_p\Delta_1\theta + p\Delta v = 0. \tag{4}$$

Since the transformations are infinitesimal, we have

$$\Delta_2\theta = \frac{\Delta_1\theta}{\Delta v}\Delta v = \left(\frac{\partial\theta}{\partial v}\right)_p \Delta v, \tag{5}$$

and

$$\Delta_2\theta = \frac{\Delta_2\theta}{\Delta_2 p}\frac{\Delta_2 p}{\Delta v}\Delta v = \left(\frac{\partial\theta}{\partial p}\right)_\epsilon \left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta_v. \tag{6}$$

$$= \eta \left(\frac{\partial p}{\partial v}\right)_\epsilon \Delta v.$$

Eliminating $\Delta_1\theta$, $\Delta_2\theta$ and Δv from (4), we have

$$(C_p - C_v)\left(\frac{\partial\theta}{\partial v}\right)_p - p + \eta C_v \left(\frac{\partial p}{\partial v}\right)_\epsilon = 0. \tag{7}$$

An expression for $(\partial p/\partial v)_\epsilon$ may be obtained as follows. For all transformations we have

$$dp = \left(\frac{\partial p}{\partial\theta}\right)_v d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta dv. \tag{8}$$

Hence

$$1 = \left(\frac{\partial p}{\partial\theta}\right)_v \frac{d\theta}{dp} + \left(\frac{\partial p}{\partial v}\right)_\theta \frac{dv}{dp}. \tag{9}$$

For a free-expansion (9) becomes

$$1 = \left(\frac{\partial p}{\partial\theta}\right)_v \left(\frac{\partial\theta}{\partial p}\right)_\epsilon + \left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial p}\right)_\epsilon, \tag{10}$$

or

$$\left(\frac{\partial p}{\partial v}\right)_\epsilon = \frac{\left(\frac{\partial p}{\partial v}\right)_\theta}{1 - \eta\left(\frac{\partial p}{\partial\theta}\right)_v}. \tag{11}$$

The elimination of $(\partial p/\partial v)_\theta$ from (7) and (11) gives

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{p}{C_v}\left(\frac{\partial v}{\partial \theta}\right)_p + \frac{\eta\left(\frac{\partial p}{\partial \theta}\right)_v}{1 - \eta\left(\frac{\partial p}{\partial \theta}\right)_v}. \tag{12}$$

The expressions for γ usually derived in text-books on physics are equivalent to the first two terms of the right-hand member of (12). By means of it and of certain assumptions regarding the application of the kinetic theory of gases, it is shown that for cases where such assumptions are realized the limiting values of γ are 1 and $1\frac{2}{3}$. Equation (12), however, is a perfectly general expression. It reduces to the more common expression for small pressures where $(\partial p/\partial \theta)_v$ is small and the term containing η may be disregarded. The writer has not seen elsewhere any expression similar to (12).

Equation (12), when combined with the following well-known relation deduced in texts on thermodynamics

$$C_p - C_v = \theta\left(\frac{\partial p}{\partial \theta}\right)_v\left(\frac{\partial v}{\partial \theta}\right)_p, \tag{13}$$

gives

$$\eta = \frac{\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p}{\frac{\gamma}{\gamma - 1}\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p}\left(\frac{\partial \theta}{\partial p}\right)_v. \tag{14}$$

Expression of μ as a function of γ.—In texts on thermodynamics the following equation for the Joule-Kelvin effect is derived:

$$\mu = \frac{\theta\left(\frac{\partial v}{\partial \theta}\right)_p - v}{C_p}. \tag{15}$$

Equations (13) and (15) lead directly to the following

$$\mu = \frac{\gamma - 1}{\gamma}\frac{\theta - v\left(\frac{\partial \theta}{\partial v}\right)_p}{\theta\left(\frac{\partial p}{\partial \theta}\right)_v}. \tag{16}$$

Equations (14) and (16) are the two relations, the application of which form certain of the main subdivisions of this paper.

III. The Free-Expansion and Joule-Kelvin Effects in Air.

Inspection of Available Data.—In order to apply equations (14) and (16), there are needed experimental data regarding γ, the interrelations of p, v, θ and their partial derivatives $(\partial p/\partial\theta)_v$ and $(\partial v/\partial\theta)_p$. γ for air may be obtained from data by Witkowski,[26] by Koch,[24] or from data by Joly[27] and Lussana.[28] Witkowski first computed C_p and C_v and then γ. C_p was obtained from the relation

$$\left(\frac{\partial C_p}{\partial p}\right)_\theta = -\theta\left(\frac{\partial^2 v}{\partial\theta^2}\right)_p. \tag{17}$$

C_v was obtained by means of (13). Values of γ were then computed for various temperatures ranging from 0° C. to −140° C., and for pressures up to about 130 atmospheres. Later by Kundt's velocity of sound method, he measured γ directly under pressures up to 100 atmospheres and at 0° C. and −78.5° C. These results, though noticeably higher, agree quite well with the computed results, as may be seen by an inspection of Table II. Koch's results were likewise obtained by Kundt's velocity of sound method. In his experiments the pressure varied from 1 to 200 atmospheres. The temperatures were 0° C. and −79.3° C. His results agree well with Witkowski's. Joly determined C_v for air by means of his well-known, differential, steam-calorimeter method for various temperature intervals all above 0° C. and for pressures up to about 100 atmospheres. Average values of C_p for air were determined by Lussana for various intervals of temperature between 0° C. and 200° C. and for various pressures up to 100 atmospheres. These values of C_v and C_p and the values of $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$ obtained by Amagat from his experiments on the compressibility of air, have been shown by Amagat to be quite inconsistent with one another. Data by Joly and Lussana have therefore not been relied upon in this work. The writer has seen only an abstract of Witkowski's paper in which the Kundt method of measuring γ was detailed. For the above reasons and for the added reason that the data by Koch seemed to have been obtained with great care, Koch's data have been used in the following computations. The values obtained from Koch's paper are to be found in Table II., column 7.

For the determination of the interrelations of p, v, and θ and the partial derivatives $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$, there exist the works of Amagat,[29] Witkowski[17] and Koch[24]. Amagat's data relate to temperatures above 0° C. and can not be used in connection with the data on γ selected. Witkowski's results on the compressibility of air cover the range of temperatures and pressures of the γ data selected. Moreover, the values of the product pv as a function of p at 0° C. and − 78.5° C. have been

fairly well verified by Koch. Witkowski's data on the compressibility of air have therefore been made use of.

Method of Handling p, v, θ data.—In applying equations (14) and (16), $(\partial v/\partial\theta)_p$ and $(\partial p/\partial\theta)_v$ do not merely appear by themselves but also in the expressions $v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v$. The values for these expressions were obtained as follows: Consider

$$(pv)_\theta = f(p). \tag{18}$$

The derivation of (18) with respect to p gives on rearranging

$$\left(\frac{\partial p}{\partial v}\right)_\theta = -\frac{p}{v - f'(p)}. \tag{19}$$

Likewise we may consider

$$(v)_p = F(\theta). \tag{20}$$

Whence

$$\left(\frac{\partial v}{\partial\theta}\right)_p = F'(\theta), \tag{21}$$

and

$$v\left(\frac{\partial\theta}{\partial v}\right)_p = \frac{F(\theta)}{F'(\theta)}. \tag{22}$$

Since

$$\left(\frac{\partial p}{\partial\theta}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial\theta}\right)_p, \tag{23}$$

$$\theta\left(\frac{\partial p}{\partial\theta}\right)_v = \frac{p\theta F'(\theta)}{v - f'(p)}. \tag{24}$$

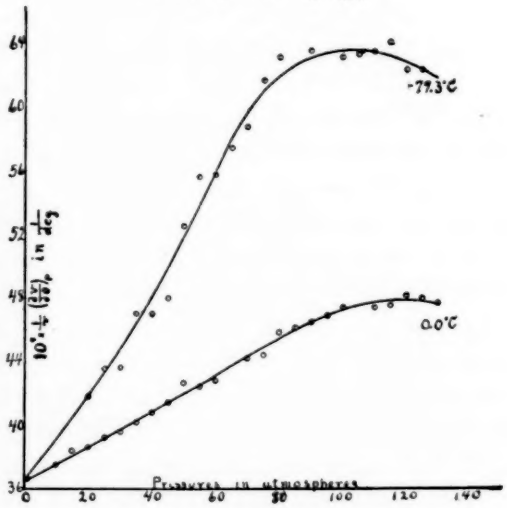

Fig. 2.

Variation of $\frac{1}{v}\left(\frac{\delta v}{\delta\theta}\right)_p$ with pressure for air.

For air at various pressures and at 0° C. and − 79.3° C., $f'(p)$ and $F'(\theta)$ were obtained from Witkowski's data by graphical means. The individual values of the reciprocals of $v(\partial\theta/\partial v)_p$ which were obtained together with the smoothed curves are shown in Fig. 2. The values used were taken from these curves.

Results from Data by Witkowski and Koch.—Certain data and computations leading to the values of μ and η are included in Table II. The

TABLE II.

Computations for μ and η of air using data obtained by Witkowski and by Koch. Air at 0° C.

p	pv	$\log\left[-\left(\frac{\partial p}{\partial v}\right)_\theta\right]$	$\log\left(\frac{\partial v}{\partial \theta}\right)_p$	$\theta - v\left(\frac{\partial \theta}{\partial v}\right)_p$	$\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
10	.9951	1.9997	$\bar{4}$.5737	7.7	.23	1.435	.228	.259	.023
15	.9923	2.3519	.4026	11.4	.52	1.448	.227	.260	.035
20	.9897	2.6017	.2824	15.0	.92	1.460	.226	.259	.046
25	.9869	2.7958	.1906	18.6	1.48	1.472	.225	.265	.059
30	.9842	2.9546	.1160	22.0	2.13	1.483	.223	.263	.071
40	.9793	3.2057	.0005	28.7	3.92	1.508	.220	.270	.090
50	.9754	3.4010	$\bar{3}$.9134	35.1	6.35	1.533	.217	.275	.127
60	.9723	3.5614	.8440	41.2	9.48	1.557	.212	.278	.158
70	.9701	3.6969	.7881	47.0	13.46	1.582	.207	.281	.192
80	.9688	3.8160	.7392	52.5	18.10	1.603	.201	.279	.226
90	.9681	3.9212	.6984	57.7	23.8	1.625	.195	.278	.264
100	.9681	4.0155	.6598	61.3	29.4	1.645	.186	.270	.294
110	.9690	4.1034	.6244	64.0	36.0	1.663	.175	.263	.327
120	.9710	4.1838	.5882	64.5	41.6	1.682	.162	.253	.347
130	.9738	4.2602	.5530	63.6	47.7	1.700	.147	.243	.367
			Air at − 79.3° C.						
1	.708	.1488	$\bar{3}$.5643	.8		1.405	.230		
10	.690	2.1500	$\bar{4}$.5866	15.1	.57	1.463	.452	.447	.057
15	.681	2.5022	.4236	22.6	1.34	1.495	.458	.463	.089
20	.672	2.7520	.3124	30.1	2.48	1.530	.464	.476	.124
25	.664	2.9459	.2299	37.4	4.05	1.567	.466	.489	.162
30	.655	3.1046	.1644	44.3	6.01	1.602	.462	.492	.200
40	.638	3.3541	.0664	56.9	11.04	1.681	.452	.487	.276
50	.620	3.5483	.0062	71.6	19.48	1.765	.447	.493	.390
60	.606	3.7071	$\bar{3}$.9554	81.9	29.01	1.857	.424	.474	.483
70	.587	3.8499	.9209	93.1	44.4	1.950	.397	.457	.634
80	.573	3.9819	.8783	99.0	60.5	2.044	.360	.431	.756
90	.562	4.0981	.8340	102.3	75.8	2.125	.327	.397	.842
100	.554	4.2097	.7900	104.0	93.7	2.200	.293	.368	.937
110	.550	4.3122	.7478	104.4	112.5	2.290	.264	.344	1.023
120	.547	4.3998	.7072	104.3	128.0	2.370	.243	.324	1.067
130	.546	4.4804	.6683	103.7	143.0	2.460	.226	.308	1.100

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

value of the ice point for this table was taken as 273.2° K. The value used for the other and later computation was 273.1° K. The variations produced by not using the latter value throughout are inappreciable, hence Table II. has not been corrected in this respect. The computed free-expansion and Joule-Kelvin effects are indicated in Fig. 3 by open circles.

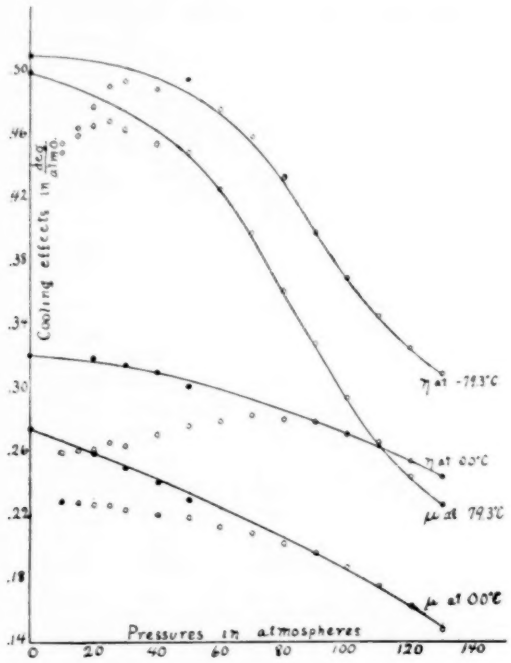

Fig. 3.

Variation with pressure of the free-expansion (η) and Joule-Kelvin (μ) effects in air at 0.0° C. and = 79.3° C.

Results based on

Witkowski's data ..... ○

K. Onnes's equation ..... ●

K. Onnes's Equation.—The values in Fig. 3 indicated by circles with filled centers are obtained by using Kamerlingh Onnes's[16] empirical equation representing the isothermals of air at 0° C., 20° C. and 99.4° C. for pressures up to about 50 atmospheres and Koch's data on γ. The equation given by Kamerlingh Onnes is

$$pv = A + \frac{B}{v} + \frac{C}{v^2}, \tag{25}$$

where v is expressed in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, p in atmospheres, and A, B and C

are functions of θ, the individual values of A, B and C are as shown for the given temperatures in Table III.

TABLE III.

Constants for Kammerlingh Onnes's empirical equation for air.

T	A	B	C
0.0° C.	1.0006	$-.0_5 57440$	$.0_5 29594$
20.0° C.	1.0739	− 40495	30178
99.4° C.	1.3647	+ 25057	35669

Results from K. Onnes's Equation and Koch's Data.—The computations for μ and η, excepting those for zero pressure, differ in this case from those in which the p, v, θ relations were obtained from Witkowski's data in that $(\partial p/\partial v)_\theta$ was obtained in this case by differentiation. Table IV. indicates these results.

TABLE IV.

Computations for μ and η of air at 0° C. using Kammerlingh Onnes's equation of state and γ data by Koch.

p	pv	$\log\left[-\left(\frac{\partial p}{\partial v}\right)_\theta\right]$	$\log\left(\frac{\partial v}{\partial \theta}\right)_p$	$\theta - v\left(\frac{\partial \theta}{\partial v}\right)_p$	$\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
0	1.0006	———	———	——	———	———	.273	.320	.000
10	.9952	2.0000	$\bar{4}.5759$	8.9	.29	1.435	.262	.322	.029
20	.9902	2.6022	.2869	17.3	1.16	1.448	.258	.318	.058
30	.9859	2.9550	.1220	24.9	2.62	1.460	.249	.313	.087
40	.9822	3.2060	.0073	31.7	4.64	1.472	.239	.308	.116
50	.9790	3.4009	$\bar{5}.9199$	37.7	7.18	1.483	.229	.300	.144

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

Values for μ and η at Zero Pressure.—The values for μ_0 and η_0 at $p = 0$ were obtained by a method indicated for μ_0 by J. P. Dalton.[16] The method of obtaining η_0 is outlined briefly here. By means of (13), (14) may be rewritten as

$$\eta = \frac{\theta - p\left(\frac{\partial \theta}{\partial p}\right)_v}{C_p\left(\frac{\partial \theta}{\partial v}\right)_p - p}. \tag{26}$$

By the direct processes of calculus and by the substitution of $v = \infty$, we get

$$\eta_0 = \frac{1}{C_{p0} - \frac{\partial A}{\partial \theta}} \frac{\theta\left(\frac{\partial B}{\partial \theta}\right) - B}{A}. \tag{27}$$

The analogous value for μ_0 obtained from (15) is

$$\mu_0 = \frac{\theta \frac{\partial B}{\partial \theta} - 2B}{C_{p0} A}. \tag{28}$$

The well established value of C_{p_0} for air under low pressures is very closely $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$, or in the units consistent with those chosen for p and v in this paper $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.} \times \text{deg.}}$.

It is to be noticed that the two sets of values for μ and η included in Tables II. and IV. differ considerably, the greatest variations occurring with the smaller pressures. This is evidently due to the smallness of the quantities $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$. The entire differences result from very small but noticeable variations in corresponding values of $(\partial v/\partial\theta)_p$. This source of uncertainty is plainly much less effective at the higher pressures.

Results for μ at o° C.—The value obtained for the Joule-Kelvin effect at zero pressure μ_0 at o° C. from Kamerlingh Onnes's equation agrees very closely, as has been shown by J. P. Dalton, with the experimental value obtained by Joule and Kelvin and with his own experimental value. It also agrees very well with the computed value obtained by using Buckingham's equation in which he expressed in a single formula the results of all experimental Joule-Kelvin effects for various substances under moderate pressures, as a function of the temperature. Each of these values closely approximates $.273 \frac{\text{deg.}}{\text{atmo.}}$. This value has therefore been selected on the plot Fig. 3, as the starting point for the curve at o° C. J. P. Dalton's experimental results for the porous plug expansion of air through a glass reduction-valve are very well represented by the equation,

$$T_1 - T_2 = .273(p_1 - 1) - .000208(p_1^2 - 1). \tag{29}$$

p_1 represents the initial pressure of the air, a quantity which in his experiments reached a pressure of 43 atmospheres. T_1 the initial temperature was o° C. The final pressure was that of the atmosphere. T_2 represents the final temperature. The ratio $\frac{T_1 - T_2}{p_1 - 1}$, if platted on Fig. 2 would start with the same initial value for μ_0 as chosen and would continue from there in a line lying approximately half way between the line $\mu = .273 \frac{\text{atmo.}}{\text{deg.}}$ and a line passing through the points determined by

Kamerlingh Onnes's equation and the γ data of Koch. When it is remembered that the results of Dalton represent effects from finite expansion of considerable magnitude and that the mean temperatures during such expansions are, for the higher pressures especially, noticeably less than 0° C., for which temperatures the Joule-Kelvin effect becomes greater, it will be seen that the deviation spoken of above is to be expected. Moreover, it may be readily shown that this deviation agrees in magnitude with what is obtained by some rather rough computations. For an initial pressure of 40 atmospheres, (29) gives for T_2 a value of $-$ 10.3° C. If now (1) may be taken as approximately true, and if it is further assumed that the value of μ for 0° C. and atmospheric pressure is $.273 \frac{\text{deg.}}{\text{atmo.}}$, it follows that the value of μ for $-$ 10.3° C. and atmospheric pressure is $.294 \frac{\text{deg.}}{\text{atmo.}}$. The value for μ at 0° C. and 40 atmospheres, according to data based on Kamerlingh Onnes's equation, is $.239 \frac{\text{deg.}}{\text{atmo.}}$. For air initially at 0° C. and 40 atmospheres, expanding through a valve as in J. P. Dalton's experiment to atmospheric pressure, an average value for μ might be expected which is near the mean of the extreme values given above. This computed average for μ, $.266 \frac{\text{deg.}}{\text{atmo.}}$, agrees very well with the value to be obtained from (29), $.264 \frac{\text{deg.}}{\text{atmo.}}$. Because of these agreements, it has been assumed in drawing the curve for μ at 0° C. that the values computed with the aid of Kamerlingh Onnes's equation of state are correct. The general trend of these values are such as to show agreement with the values of μ obtained for the higher pressures using Witkowski's data. It might be expected that these latter values would not be far from the correct values, since here, as may be seen in Table II., small errors entering into $\theta - v(\partial\theta/\partial v)_p$ would cause but small errors in the computed results for μ. Hence the further continuance of the curve. The curve for μ at 0° C. is well represented by (30).

$$\mu_{T=0} = .273 - .00076p - .0000012p^2. \tag{30}$$

Results for μ at $-$ 79.3° C.—In drawing the curve for μ at $-$ 79.3° C., the value given by Buckingham's equation was selected as being the most probable value for μ at zero pressure. This value of $.498 \frac{\text{deg.}}{\text{atmo.}}$ was found to agree very well with the value $.486 \frac{\text{deg.}}{\text{atmo.}}$ for $-$ 78.5°

which was obtained by using as before, equations similar to (25) and Witkowski's experimental value of C_p .2375 $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ or .01273 $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$. The equations used here however were of the type

$$pv = A + B/v. \tag{31}$$

A and B have the values indicated in Table V. at the stated temperatures

TABLE V.

Constants for equation (31).

T	A	B
0.0° C.	1.0006	−.000574
− 78.5	.7130	−.001193
−103.5	.6214	−.001473

when as before p is expressed in atmospheres and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$. The values of A and B relating to 0° C. have been given by Kamerlingh Onnes. The remaining values of A were determined on the supposition that at zero pressure air rigorously obeys the perfect gas law. The remaining values for B were determined with the additional supposition that Witkowski's data on the values of v for air at − 78.5° C. and − 103.5° C. for a pressure of 20 atmospheres are correct. These values are respectively .03389 and .02848 $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$.

Results for η at 0° C.—In drawing the curve for the free-expansion effect η of air at 0° C., preference was given at small pressures to the values computed with the aid of Kamerlingh Onnes's equation and constants, because they had given very nearly the correct results for the Joule-Kelvin effect at the same temperature and pressure. It is, of course, to be borne in mind that, even if an equation of state should indicate correct values for the Joule-Kelvin effect for any pressure and temperature, the computed free-expansion effects as determined by that equation of state might deviate far from the true values. If, however, in addition to leading to the correct Joule-Kelvin effects, the equation correctly represents the isothermals, then as has been shown by Bakker,[30] the equation will lead to correct free-expansion effects. As in connection with the Joule-Kelvin effect and for a similar reason, we may expect that the computed free-expansion effects based on Witkowski's data, in the case of high pressures, will not deviate far from the true values.

Here $\theta(\partial p/\partial\theta)_v - p$ is the term which practically determines the accuracy of the computed results. The writer knows of no direct determinations of η which might be used here. The curve for η at 0° C. is well represented by (32).

$$\eta_{T=0} = .320 - .00018p - .0000032p^2. \tag{32}$$

Results for η at $-79.3°$ C.—In drawing the curve for the free-expansion effect η at $-79.3°$ C., the value for zero pressure was chosen as follows: The value computed with the aid of equation (31) and the accompanying constants for zero pressure and $-78.5°$ C. was $.496\frac{\text{deg.}}{\text{atmo.}}$. Since the Joule-Kelvin effect for zero pressure and $-78.5°$ C. computed from the same data differed by $.012\frac{\text{deg.}}{\text{atmo.}}$ from the value given by Buckingham's equation for $-79.3°$ C., and since the variations of μ and η with temperature seem to be about the same, as the general trend of the curves drawn indicate, it was assumed, that the value for η_0 at $-79.3°$ C. was higher than the computed value at $-78.5°$ C. by $.012\frac{\text{deg.}}{\text{atmo.}}$, making the value selected $.508\frac{\text{deg.}}{\text{atmo.}}$.

Agreement with Witkowski's Results.—There has been mentioned the work of Witkowski.[17] He started with a number of experimentally determined relations between p, v and θ, and with the experimental conclusion that C_p for air at 1 atmosphere is independent of the temperature, computed isenthalpic and isenergic curves for air embracing a region from 0° C. to $-140°$ C. and from zero pressure to 130 atmospheres. Graphical methods were largely used. The slopes of these curves give directly the Joule-Kelvin and the free-expansion effects. The writer has included in Table VI. a number of values for μ and η thus obtained together with the corresponding values from the present work. Excepting for the lower pressures, the agreement is good. As has been previously suggested, the variations here are undoubtedly largely due to the smallness of the corresponding values for $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_p - p$. Witkowski himself ascribed the variation of his results from those of Joule and Kelvin to the uncertainties entering into his graphical calculations.

Internal Work of Expansion.—It is of considerable interest in this connection to consider the relative magnitudes of the effects of the internal forces, intramolecular as well as intermolecular, which give rise to the free-expansion and to a large extent to the Joule-Kelvin effects. This

TABLE VI.

Corresponding values of μ and η according to Witkowski and to Worthing.

T in °C.	Values of μ in $\frac{\text{deg.}}{\text{atmo.}}$			T in °C.	Values of η in $\frac{\text{deg.}}{\text{atmo.}}$		
	p in Atmos.	(Witkowski)	(Worthing.)		p in Atmos.	(Witkowski.)	(Worthing.)
0.0	40	.20	.242	0.0	50	.23	.303
	70	.23	.215		84	.265	.282
	113	.175	.175		121	.252	.252
−79.3	0	.515	.498	−79.3	19	.491	.505
	15	.496	.490		38	.509	.496
	30	.476	.476		55	.500	.480
	43	.468	.460		71	.468	.452
	57	.448	.430		88	.424	.403
	69	.400	.397		104	.358	.358
	83	.365	.349		122	.323	.322
	97	.308	.303				
	112	.248	.260				
	130	.222	.226				

may best be done by determining the ratio of the work done against these internal forces ΔW_1 to that done against external forces ΔW_2 when a gas undergoes an infinitesimal, reversible, isothermal expansion. The internal work for such an expansion is evidently equal to the change in internal energy, which in turn is equal to the heat, measured in appropriate units, which must be added to the substance following the free-expansion from the initial to the final volume to bring it without changing the volume to the initial temperature.

$$(33) \qquad \Delta W_1 = (\Delta\epsilon)_\theta = -C_v\eta(\Delta p)_v = -C_v\eta\left(\frac{\partial p}{\partial v}\right)_v \Delta v.$$

With the aid of (11), (12) and (13), there follows

$$(34) \quad \Delta W_1 = \left(\frac{\partial \epsilon}{\partial v}\right)_\theta \Delta v = -\frac{C_v\eta\left(\frac{\partial p}{\partial v}\right)_\theta}{1-\eta\left(\frac{\partial p}{\partial \theta}\right)_v}\Delta v = \left[\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p\right]\Delta v.$$

The desired ratio of the internal work to the external work is given by

$$(35) \qquad \frac{\Delta W_1}{\Delta W_2} = \frac{\theta\left(\frac{\partial p}{\partial \theta}\right)_v - p}{p}.$$

This relation is true for all infinitesimal, reversible expansions in which the accompanying changes in p are infinitesimal. Values for $\Delta W_1/\Delta W_2$

for air have been computed and are to be found in the last columns of Tables II. and IV. The results have been platted in Fig. 4. In Fig. 4 only those points have been platted for which the corresponding computed values of μ and η were found to fall closely on the platted curves of Fig. 3. What has been noted previously regarding the uncertainties in $\theta(\partial p/\partial\theta)_v - p$ at low pressures, applies equally here. The changes in $\Delta W_1/\Delta W_2$ with pressure and with temperature are very evident, the ratio for the lower temperature and the higher pressures being greater than unity.

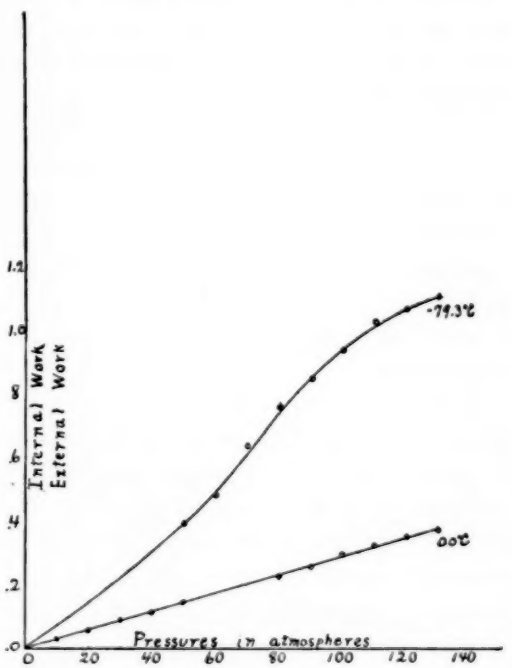

Fig. 4.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ in air for infinitesimal, reversible, isothermal expansions.

Results based on
Witkowski's data..... ○
K. Onnes's equation..... ●

Conclusions Regarding η, μ and $\Delta W_1/\Delta W_2$ of Air.— The plats show that in air for the region considered:

1. The free-expansion effect η is greater than the Joule-Kelvin effect μ for the same pressure and temperature.

2. The absolute difference between η and μ for the same pressure and temperature increases with increasing pressure.

3. Both η and μ are greater for the lower temperature than for the higher temperature.

4. Both η and μ beginning with low pressures, decrease with increasing pressures, the rate of decrease being the greater, the greater the pressure.

5. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\Delta W_1/\Delta W_2$ is greater at $-79.3°$ C. for a given pressure than at 0° C.

6. The ratio $\Delta W_1/\Delta W_2$ starts with zero values at zero pressure and increases with pressure, and in the case of the lower temperature, reaches a value greater than unity.

IV. THE DETERMINATION OF γ FOR CO_2 AS A FUNCTION OF THE PRESSURE AND THE TEMPERATURE.

Consideration of Existing Data.—There exist many determinations of γ for CO_2 under atmospheric pressure. There exist for pressures considerably greater, so far as the writer knows, only the computations of Amagat,[13] in which he combines the determinations of C_v made by Joly[32] with his own determinations of the interrelations of p, v and θ. His own work enabled him to determine $\theta(\partial p/\partial\theta)_v(\partial v/\partial\theta)_p$ for the gas at any desired pressure and temperature. By the application of (13), C_p and then γ were determined; first at varying pressures for a density of the CO_2 of .124 gr./cm.^{3}, then at varying pressures for a temperature of 50° C. He obtained various values for γ which showed that quantity to increase noticeably with increasing pressure and with decreasing temperature. For a temperature of 50° C. and a pressure of 100 atmospheres, he found γ to be 4.633. Unfortunately the results are such that it is impossible to check them by comparing them with other determined values at one atmosphere.

At about the same time there appeared papers by Lussana[33] on the values of C_p for CO_2 at about the same pressures and temperatures. Evidently his results might be combined with Amagat's, C_v determined and then γ; or his results might be combined with Joly's directly and γ thus determined. The writer has attempted the latter. It has been necessary to plat the given values of C_p and C_v in order to get values for C_p and C_v under the same conditions. Table VII. includes the results

TABLE VII.

γ for CO_2 from data by Joly and by Lussana.

p	30°			50°			80°		
	C_p	C_v	γ	C_p	C_v	γ	C_p	C_v	γ
10	.297	.169	1.76	.259	.169	1.53	.250	.168	1.49
20	.301	.173	1.75	.263	.172	1.53	.253	.171	1.48
30	.318	.179	1.72	.268	.177	1.52	.258	.175	1.48
40	.318	.184	1.73	.276	.182	1.52	.264	.180	1.47

p is expressed in atmospheres. C_p and C_v are expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of such computations. Joly's conclusion, that for densities less than .124 gr./cm.^{3} C_v for CO_2 is practically independent of the temperature, was assumed as correct. There are only a few values which may be compared with those mentioned above as having been obtained by Amagat. There is but very little agreement between the two sets of

determinations. Moreover the variations of γ in Table VII. are such as would indicate values of γ under atmospheric pressure which are very different from the generally accepted values. There is evident need of further determinations of γ for CO_2 for various pressures and temperatures.

Methods of Measuring γ for Gases under High Pressures.—There are several methods of determining γ which are practicable when applied to a gas under high pressures. There are (1) the thermodynamic method used by Witkowski as described briefly in an earlier part of the present paper; (2) the separate determination of C_p and C_v; (3) the determination of C_p and the consequent computation of C_v by equation (13); (4) the determination of C_v and the consequent determination of C_p by equation (13); (5) the method of Jamin and Richard[34] in which the isopiestic and isometric changes in temperature of a gas heated by a wire carrying an electric current is measured; (6) the method of Assmann,[35] in which there is observed the period of vibration of a system in a closed glass tube composed of a mass of the gas separated into two parts by means of a column of mercury; (7) the velocity of sound method; (8) the method of Lummer and Pringsheim[36] so modified as to apply to gases far removed from the state of perfect gas; and (9) the method of Maneuvrier,[37] a null method based on the same fundamental principles as the method commonly called after Clement and Desormes.

Reasons for Choosing the Method Selected.—The thermodynamic method of Witkowski might be applied to the data given by Amagat for CO_2. There would be required in addition however the variations of C_p or C_v with temperature at a given pressure such as atmospheric. Such determinations as these have been made but there is a great lack of consistency in the data. It has not seemed desirable to make use of this method in the present case. The next three methods necessitate the measurement of C_p, C_v or both for various pressures and temperatures. These are very difficult undertakings. Moreover, as they have already been measured by Joly and Lussana as noted above, and with very probable, serious errors as is suggested by Table VII., none of these three methods has been used in the present work. Jamin and Richard's method would undoubtedly be hard to realize under high pressure, especially in the carrying out of an isopiestic heating. Assmann's method might well yield good results, when all allowances are made for disturbing factors. The velocity of sound method has been used by Witkowski and by Koch for air with fair agreement of results with each other and with the former's results by the thermodynamic method. This method has been criticized by J. W. Capstick,[38] and by J. H. Jeans,[39] on account of a lag in the

adjustment of the intermolecular and intramolecular energies of a gas on the passage of a sound wave through the gas. In Chapter XVI. of his "The Dynamical Theory of Gases" he concluded that any such lag in adjustment, provided that a certain supposition is true, "is in every way imperceptible." The method of Maneuvrier seemed free from this serious objection. It has been used. Practically, in Maneuvrier's method the compressions are no more reversible than those in sound experiments. Time, however, is given in this method for the practical balancing of the intramolecular and the intermolecular energies before actual measurements are made. The apparatus which was constructed for this work has been so designed as to make possible measurements according to a modification of Lummer and Pringsheim's method. However, time has not been found available for the perfection of this method, and consequently no measurements of that kind have been made.

Maneuvrier Method.—The method of Maneuvrier is based on a theorem due to Reech,[40] which is applicable to any substance whatever. A simple derivation of the equation expressing this theorem follows. Let AB, AC, AD and DB, Fig. 1, represent in this instance respectively infinitesimal reversible adiabatic, isothermal, isopiestic and isometric changes. Consider the change in internal energy which takes place when a substance is carried around the cycle $ADBA$. We have then

$$(C_p\Delta_1\theta - p\Delta v) + C_v(\Delta_2\theta - \Delta_1\theta) + p\Delta v = 0. \tag{36}$$

The two following relations are evident.

$$\Delta_2\theta = \left(\frac{\partial\theta}{\partial v}\right)_Q \Delta v. \tag{37}$$

$$\Delta_1\theta = \left(\frac{\partial\theta}{\partial v}\right)_p \Delta v. \tag{38}$$

There follows at once

$$\frac{C_p - C_v}{C_v}\left(\frac{\partial\theta}{\partial v}\right)_p = -\left(\frac{\partial\theta}{\partial v}\right)_Q, \tag{39}$$

or

$$\gamma = 1 - \left(\frac{\partial v}{\partial\theta}\right)_p \left(\frac{\partial\theta}{\partial v}\right)_Q. \tag{40}$$

By a process very similar to that involved in (8), (9) and (10), we get

$$\left(\frac{\partial\theta}{\partial v}\right)_Q = \left(\frac{\partial\theta}{\partial v}\right)_p + \left(\frac{\partial\theta}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_Q. \tag{41}$$

The application of (8) to an isopiestic process gives

$$\left(\frac{\partial v}{\partial\theta}\right)_p \left(\frac{\partial\theta}{\partial p}\right)_v = -\left(\frac{\partial v}{\partial p}\right)_\theta. \tag{42}$$

Equations (40), (41) and (42) give at once

$$\gamma = \left(\frac{\partial p}{\partial v}\right)_Q \left(\frac{\partial v}{\partial p}\right)_\theta, \tag{43}$$

which is the equation expressing Reech's theorem. In case (43) is applied to finite changes in which the changes in specific volume are small and equal, we have as a first approximation

$$\gamma = \frac{\Delta p_Q}{\Delta p_\theta}. \tag{44}$$

This is the form which has been used in the present work.

It was originally planned, and the apparatus was constructed with the aim in view of measuring both Δp_Q and Δp_θ directly with the apparatus. This general method was attempted, though no satisfactory results were obtained thereby. After repeated failures to get consistent values of γ, the plan was modified. According to this method Δp_Q was measured as planned; Δp_θ, however, was computed. The methods of obtaining Δp_Q and Δp_θ will be considered later.

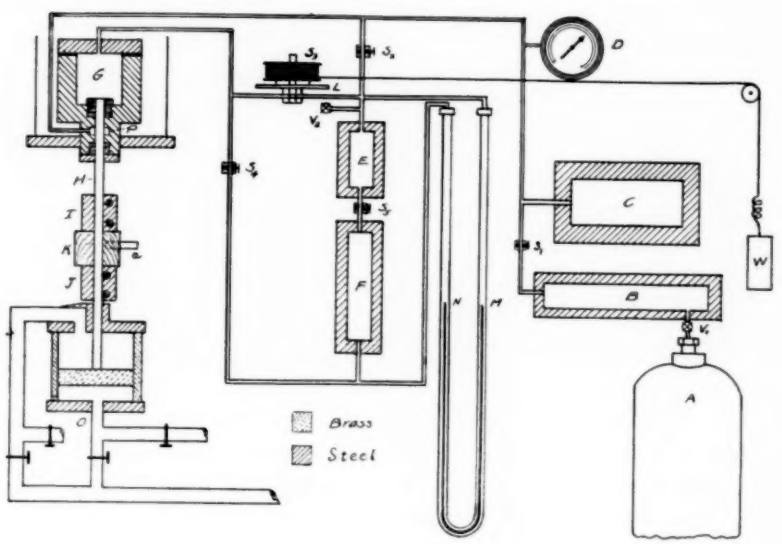

Fig. 5.

Apparatus.—The apparatus and the method of experimentation may be seen from an inspection of Fig. 5 (see also Plate I.) which represents the essential portions of the apparatus as finally connected and used. In general the arrangements and the materials have been so chosen as to withstand with safety pressures of 100 atmospheres though the actual

highest pressure attained in these experiments was about 57 atmospheres. A represents the tube containing CO_2 under pressure which in the experiments to be considered was the source of the gas and of the pressure. B represents a cylinder of about 250 cm.^{3} capacity containing phosphorous pentoxide sprinkled through cotton-wool for the purpose of removing the moisture from the gas passing through it. C represents a distributing chamber of about 600 cm.^{3} capacity which also served as a maintainer of the pressure in the protective system to be spoken of later. At the stop-cock S_2, the gas enters the system where it is to be experimented with. D is a Bourdon steam test-gauge reading to 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ by steps of 5 $\frac{\text{lbs. wt.}}{\text{in.}^2}$. E and F are chambers of respectively 150 cm.^{3} and 300 cm.^{3} capacity connected with the arms M and N of the differential, mercurial manometer. This manometer also served as a manoscope. The combination is the same as that used by Maneuvrier in his original work. The purposes of E and F are merely to give large volumes to the gas chambers of the manometer so that, in case a small leak should occur in either of these gas chambers, the rate of change of pressure in it should be negligible. E and F are separated by a stop-cock S_5 which in the final arrangement was not used. G is the compression chamber which contains the gas to be compressed or rarified. It has a capacity of about 300 cm.^{3} and is surrounded by a bath which contains a thermoregulator and a stirer (not shown in Fig. 5 nor in Plate I.). The volume of G can be increased or diminished at will by means of the device indicated at O which is actuated by compressed air. Chambers B, C, E, F and G are all japanned on the inner surfaces for the purpose of preservation and chamber G for the added purpose of surrounding the contained gas with a poor conductor for heat. H is a piston rod to which are clamped two stops I and J which are separated by a block of hard oak wood K. The use of different blocks of wood for K permits of different changes of volume in chamber G due to the thrusting in of the piston rod H. The lower stop J is firmly fixed to the rod H in order that, when H is in its lowest position, the volume of G is certain to be very closely a fixed amount. V_1 and V_2 are pin valves. S_1, S_2, S_3, S_4 and S_5 are stop-cocks. As already noted, S_5 was not made use of in the apparatus as finally arranged. The construction of S_3 is shown in Fig. 6. S_1, S_2, S_4 and S_5 differ from S_3 only in having the special device attached to the pin of S_3 replaced by a bar so that the pin may be rotated by hand. The pin of S_3 is rotated by a heavy weight W attached to a heavy spring which in turn is attached to a slender rope made of several strands of heavy fish-line, one end of which is wound about the wooden drum fastened to the pin of S_3. The pin of S_3 is provided with an arm L which serves

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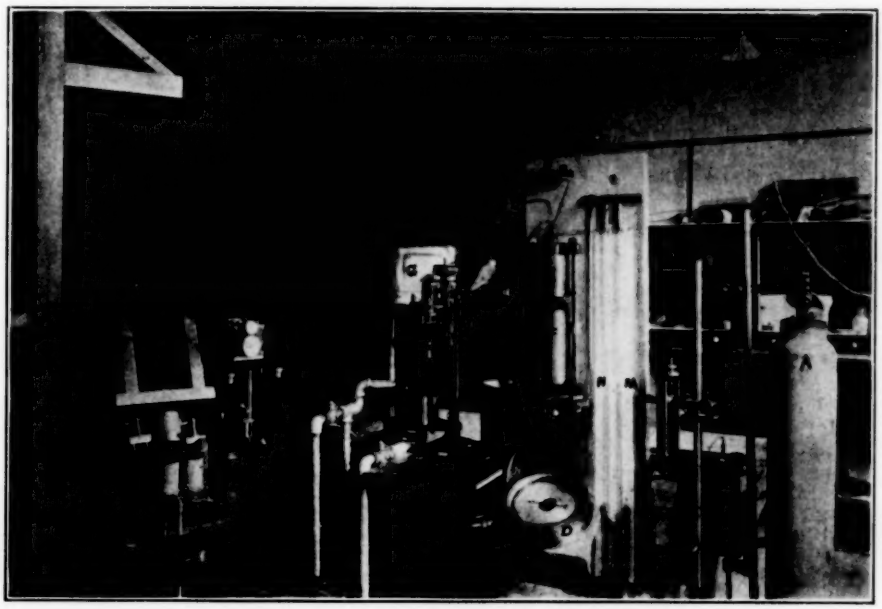

A. G. WORTHING.

PLATE I.

as a catch. The spring removes the sudden jolt that otherwise would be experienced on the sudden stoppage of the rotation of the pin of S_3. The final ground surfaces of the pin and stock were produced by grinding them in powdered quartz and, sometimes, in pumice. In Fig. 5 a small tube is shown connecting C with P. The pressure in C was always nearly equal to that in the system $EFGMN$. Consequently this connection at P together with the packing about H permits at the most, of only a slow leakage of gas into or out of G through the packing and along the surface of H. Similar tubes lead from C to all the stop-cocks. They are connected to the stop-cocks at points which lead directly to the grooves Q (Fig. 6). These grooves entirely surround the pin of the stop-cock. As before the pressure in C is distributed through the tube to Q where it

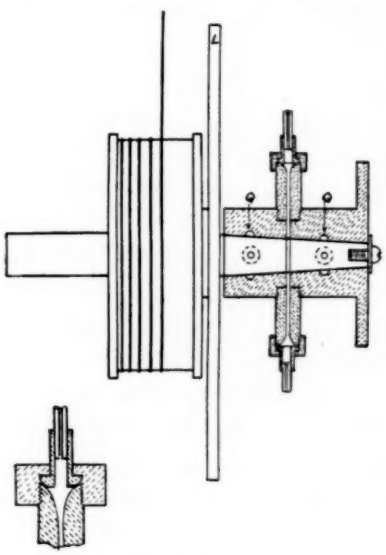

Fig. 6.

prevents the leakage of gas from or into the system $EFGMN$. The small tubing connecting the various chambers and stop-cocks is of copper. The external and internal diameters are respectively .32 cm. and .16 cm. The method of making the unions of these tubes with the other portions of the apparatus is well illustrated in Fig. 6. The external and internal diameters of the glass tubing used in the manometer are respectively .80 cm. and .30 cm. The stop-cocks are of brass, the chambers B, C, E, F and G were cut out of steel shafting.

In the method of experimentation pursued it was necessary to vary and to measure the time interval between the compression of the gas in G (Fig. 5) and the opening of the S_3. This was brought about by means of the apparatus diagrammed in Fig. 7. The block of oak wood,

K (Fig. 5) carries a projecting metal prong a. The thrusting in or out of H brings a in contact with b and c. The contact ab closes an electrical circuit through the electro-magnet d, the energizing of which releases a pendulum which in its motion closes at e an electrical circuit through the electro-magnet f, opens at g the same circuit, and breaks at h by a device not indicated, the circuit containing the electro-magnet d. The current through the circuit closed at e actuates the electromagnet f, thus releasing the catch L attached to the pin of stop-cock S_3. The weight W causes the rotation of the pin of S_3. The breaking of the circuit at g is followed by the demagnetizing of f, and the catch L, after a rotation of the pin of 180°, is caught and the rotation of the pin is suddenly stopped. In case there is contact at e when the plunger H is moved in, the electromagnets in the circuits at d and f are actuated simultaneously. Thus by having the circuit at e initially closed or broken two different time intervals may be had between the compression of the gas in G and the opening of the cock S_3. Other intervals may be had by varying W and the position of e on the pendulum apparatus. The contact ac permits a current to flow through the commutation device on the drum i of S_3 through the electromagnet of a Hipp's chronoscope (H.C.). At j this current is broken when the stop-cock S_3 is open, as may be seen by inspecting the diagram of the commutating device. S_3 is diagrammed in a closed position. Thus the chronoscope records the time elasping between the plunging in or out of H (Fig. 5) and the opening of the stop-cock S_3. Previous to July 28th, however, a slightly different method was used. The interval measured was from the plunging in or out of H to the closing of S_3.

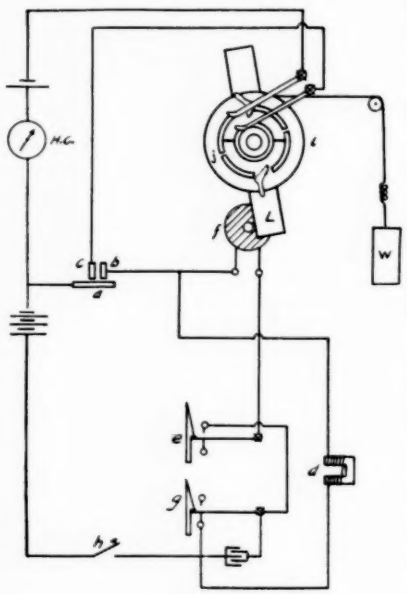

Fig. 7.

Stop-cock Difficulties.—Originally it was planned to use tallow as the stop-cock lubricant, and to have the openings to Q and the grooves Q of the stop-cocks (Fig. 6) filled with gas directly connected with that in C. It was soon very evident that this plan must be abandoned. With this arrangement, pressures of a few atmospheres could be maintained for an hour at most. A great deal of time was spent in the search for some

stop-cock fluid which should be able to withstand the high pressures. The fluid finally used was formed by dissolving approximately one part of rubber in three parts of hot pine-tar. The solution was heated and the more volatile gases driven off until the desired consistency was reached. This fluid when cool is very viscous and sticky. It was introduced in the openings leading to Q and in the grooves Q. It did quite well and often for several hours, no noticeable leaks in the apparatus could be detected. With the very highest pressures the fluid was gradually forced out between the pin and the stock of the stop-cocks. However, there was no leakage of gas to the outside, until a complete passage-way to the outside for the gas back of the rubber-tar solution had been formed. As soon as such a passage-way was formed, the desired gas pressure in C was usually very hard to maintain by the admission of gas through S_1 and it was necessary to discontinue the experiment, empty the apparatus and refill the receptacles with the rubber-tar solution. For further work with this apparatus, considerably enlarged receptacles for the stop-cock fluid should be provided.

The Experimental Determination of Δp_Q.—In the filling of the apparatus with the gas to be experimented upon, it was necessary to be sure that the gas was dry and that whatever air was in the apparatus initially was removed or nearly so. The moisture was removed by the phosphorus pentoxide in B (Fig. 5). The phosphorus pentoxide was replaced by a fresh supply several times. In each instance, that furthest from the entrance to chamber B was found when removed to be a dry powder, thus indicating that in all cases the carbon dioxide gas experimented on was free from moisture. The removal of the air was accomplished partially with a hand pump, then carbon dioxide was allowed to fill the exhausted space. This mixture of air and carbon dioxide was then pumped out and the process repeated until it was certain that not more than .05 per cent. of the gas in the apparatus was of the original air. After the desired pressure throughout the apparatus including the protective system had been reached and had become steady due to the temperature having reached a steady state, S_3 was closed. Then, depending on whether the change in the compression chamber G was to be a compression or a rarefaction, the pressure in the protective system and in E and M was increased or decreased until the expected change in pressure in the compression chamber was equal to the difference indicated by the mercury levels in M and N. Then S_4 was closed. At this stage, it is to be kept in mind, the pressure in the compression chamber G was the same as that in F and that at the upper surface of the mercury in N; and that the pressure in E was the same as that in M. Now with the rapid successive opening and closing of the valves letting compressed

air into and out from O, the gas in G was compressed or rarified due to the motion of the piston H, contact was made at ab and ac (Fig. 7), as explained above; the pin of S_3 was rotated connecting for a short space of time chambers E and G; and the time interval between the making of the contact ac and the opening of S_3 was recorded by the Hipp's chronoscope H.C. This was very quickly followed by the reverse movement of the piston H in order that there might be but a very small amount of heat lost or gained by the gas in the compression chamber as a result of the heating or cooling from the previous direct motion of H. In case the pressures in G and M were not equal on the opening of S_3, a passage of gas must necessarily have taken place through S_3; and, on the return of H to its initial position, S_4 was opened. There was a readjustment of pressure then in G, F, and N and also in E and M. When a steady state was reached, usually after a minute or so, the process beginning with the closing of S_4 was repeated. In fact it was necessary to repeat again and again until, by the automatic transference of gas through S_3 from G into E or vice versa, there should occur for at least for two successive repetitions no transference of gas from E to G or vice versa. This condition was determined by an observer looking through a cathetometer telescope at the upper mercury surface in M or in N. Whenever in the process described above there occurred a transfer of gas from G to E or vice versa, there was a shift in the mercury level. When a condition of balance obtained, no further shifting of the mercury surface could be noted, in fact no distortion of the surface could be detected. With the apparatus in working order, it usually did not require more than ten trials before the balance was obtained. The actual difference of pressure produced in the compression chamber and existing after the time interval shown by the Hipp's chronoscope, was measured on the differential manometer MN by means of the cathetometer. By varying the initial conditions at the contact e (Fig. 7), data corresponding to two time intervals may be obtained.

Now, if it may be assumed here that the change in *the change in pressure* due to heat being conducted to or from the gas in G is a linear function of the time for short intervals of time, we may obtain the change in pressure which would have occurred in G if the time interval had been infinitesimal. Let Δp_1 and Δp_2 be changes in pressure and Δt_1 and Δt_2 be the corresponding intervals of time in the above described experiment. Let Δp_0 be the change in pressure for an infinitesimal interval. Then we have

$$\Delta p_0 = \Delta p_1 - \frac{\Delta p_2 - \Delta p_1}{\Delta t_2 - \Delta t_1} \Delta t_1 . \tag{45}$$

Δp_0 is the Δp_Q of (44). Data from certain preliminary measurements obtained July 25 and platted in Fig. 8, indicate that the assumption is not far from true. Near the completion of the experimental work, other attempts were made to test (45) more carefully. In each instance, certain accidental changes occurred which made impossible the obtaining of the desired number of different intervals under conditions which would be necessary for a rigid test. Even if the assumption made is not true, the actual variation from it could hardly be such as to cause any serious error.

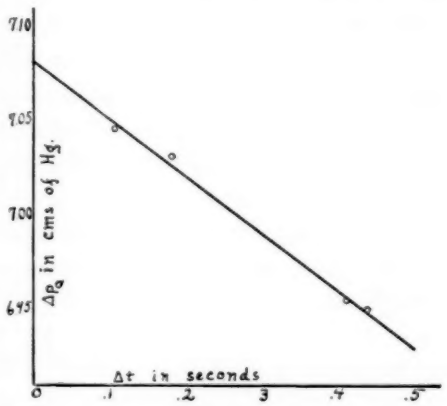

Fig. 8.

Experimental test of assumption made in (45)

It is perhaps well to note here certain precautions taken to insure accuracy. The pressure gauge was always adjusted so that the index was aligned with some desired division on the dial. The face of the gauge was always tapped lightly to insure the freedom of movement of the indicating parts. Parallax was carefully eliminated. A single division on the dial corresponded to 5 $\frac{\text{lbs. wt.}}{\text{in.}^2}$. A variation of one twentieth of a division was noticeable. This corresponds to about one sixtieth of an atmosphere. Actual trials showed that any desired pressure could be certainly obtained (assuming the gauge to be correct) to within 1.5 cm. of Hg. To prevent any errors due to the sticking of the mercury in the manometer tube, the glass tubes M and N were tapped just before and just after the compression or rarefaction in G was produced. To further eliminate such troubles, the initial pressure in E for one determination of Δp_Q for a given p and T was first made too great and for the next determination under the same conditions was made too small, in order that in the self-adjusting process there would in the first case be a slight movement of the mercury in N upwards and then in the second case downwards. The two values of Δp_Q obtained thus were always in very good agreement, they always differed in such a manner as to indicate that there was some sticking of the mercury to the manometer tubes. These differences in Δp_Q, with a few exceptions relating to measurements especially difficult, did not amount to more than .6 mm. of Hg and usually were much less. The average of two such values for Δp_Q were taken as

the observed value. When it is considered that the actual values of Δp_Q varied from 5 to 13 cm. of Hg, it will be seen that the uncertainties arising from this source will generally be quite small. In order to eliminate any errors in the measurement of Δp_Q due to leakage of gas during the measurements of the heights of the mercury columns in M and N, one observer noted during this process with the aid of a traveling microscope the slow motion, if it existed, of the mercury in column M. Corrections to the cathetometer readings for such leakages were readily made. In addition to the ordinary precautions for cathetometer work, double settings were made. If the readings from these double settings were not consistent with the difference noted on the traveling micrometer, further readings were taken.

In order that a clear idea of the method of procedure may be obtained, certain of the records for the afternoon of August 12 are presented in Table VIII., together with certain explanatory notes. C and R indicate

TABLE VIII.

Sample note book records showing experimental details for determination of Δp_Q. Aug. 12, 1910, P. M.

Movement of compressing piston with blocks no. 3 and no. 4 at K (Fig. 4).

Mean of five determinations at the beginning	1.435 cm.
Mean of five determinations at the end	1.426 "
	Av. 1.430 "

Gauge reading: $300 \frac{\text{lbs. wt.}}{\text{in.}^2}$.

Collected data:

Room Temp.	Bath Temp.	Change.	N in cm.	M in cm.	$M-N$ in cm.	Adjustment.	Interval in Sec.	Remarks.
26.6°	50.0°	C.	92.672	83.395	9.277	down	.095	?
.6	"	"	.658	.412	.246	up	.098	good
.6	"	"	.627	.430	.197	down	.070	good
.5	"	"	.610	.470	.140	down	.314	
.4	"	"	.630	.435	.195	up	.310	
.4	"	R	82.321	92.552	.231	up	.090	
.2	"	"	.340	.540	.200	down	.090	
.2	"	"	.365	.516	.151	up	.304	
.1	"	"	.390	.515	.125	down	.304	

Note book records from which N, M and interval entries of the fourth observation were taken.

N' in cm.	Chronoscope Reading.	Chronoscope Interval.	N'' in cm.	N in cm.	M in cm.	Traveling Microscope Reading in cm.
	005			92.610		8.911
32.61	163	158	32.60	.605		15
.60	322	159	.59		83.480	19
.59	475	153	.59		.480	21
.59	632	157	.59	Corrected 92.610	83.470	

respectively a compression and a rarefaction. The N and M readings are the cathetometer readings on the mercury meniscuses in tubes N and M (Fig. 5). $M \sim N$ represents the numerical difference between M and N. The adjustments "up" and "down" indicate that, in the self-adjustment of the gas pressure preceding the equilibrium, the motions of the mercury surface in N during a compression and in M during a rarefaction were "up" and "down" respectively. The "interval" measured is the time elapsing between the making of the circuit at ac (Fig. 7) and the breaking of the circuit at j. It is thus the interval between the plunging in of the piston H and the opening of stop-cock S_3 so that chambers E and G were in communication. Under remarks it is noted that the first observation was considered questionable when taken. It does not check up with the other observations from the standpoint of the variation in Δp_Q due to up and down adjustments. It has been discarded in the further computational work. The readings N' were read on a rough paper scale back of tube N with the aid of the cathetometer telescope, just before the gas in G was compressed; the readings N'' were taken in a similar manner just after. The unit of the chronoscope readings was .002 sec. The average interval was therefore .314 sec. The slight variations in the individual intervals are partially to be accounted for by the fact that the weight W (Fig. 5) was usually still being vibrated up and down somewhat by the spring above it when a new compression was about to be made. The method of obtaining the corrected N and M readings is evident. From the collected observations given, there are to be obtained as indicated above with the aid of (45) and on correcting $M \sim N$ to 0° C., data recorded in the first six columns of Table XIII. under the proper date. Nearly all such data relating to Δp_Q represent values obtained in the manner indicated above, with the exception that usually only two observations, one an "up," the other a "down" for the same interval were taken either for the rarefaction or for the compression. In computing Δp_Q by (45), the term multiplying Δt, was assumed to be the same as in the other process for which the regular four observations were taken.

The Computations for Δp_θ.—Kamerlingh Onnes[41] has given an empirical equation of state for CO_2 which is founded on Amagat's work and which represents Amagat's data with a very high degree of accuracy. The equation is of the form

$$\lambda\pi v = A + \frac{B}{\lambda v} + \frac{C}{(\lambda v)^2} + \frac{D}{(\lambda v)^4} + \frac{E}{(\lambda v)^6} + \frac{F}{(\lambda v)^8}, \tag{46}$$

where

$$\lambda = \frac{p_c v_c}{\theta_c}, \quad p_c = \frac{p}{\pi}, \quad \theta_c = \frac{\theta}{\tau} \text{ and } v_c = \frac{v}{\nu}, \tag{47}$$

v being expressed in $\frac{\text{T. N. V. Units}}{\text{gr. x mol.}}$; and where A, B, C, etc., are functions of θ such that

$$\begin{aligned} A &= a_1\tau, \\ B &= b_1\tau + b_2 + b_3/\tau + b_4/\tau^3, \\ C &= c_1\tau + c_2 + c_3/\tau + c_4/\tau^3, \\ &\cdots\cdots\cdots\cdots \\ F &= f_1\tau + f_2 + f_3/\tau + f_4/\tau^3. \end{aligned} \tag{48}$$

(46) was used in this work. It was found that in no case were there appreciable errors introduced in the present work by neglecting the terms containing D, E and F. Table IX. gives the necessary constants.

TABLE IX.

Constants for (47).

Subscript.	1	2	3	4
$10^4 a$	36.62			
$10^8 b$	173.6	−321.3	−.241.5	−82.4
$10^{11} c$	66.2	− 47.6	111.2	103.6

In the computations connected with the present work the values of v were expressed for the most part in $\frac{\text{N. V. units}}{\text{gr. mol.}}$ in order to check the computations based on K. Onnes's equation with the experimental data of Amagat.[29] In determining Δp_θ the following expansion was used

$$\Delta p_\theta = \left(\frac{\partial p}{\partial v}\right)_\theta \Delta v \left[1 + \tfrac{1}{2}\frac{\left(\frac{\partial^2 p}{\partial v^2}\right)_\theta}{\left(\frac{\partial p}{\partial v}\right)_\theta}\Delta v + \tfrac{1}{6}\frac{\left(\frac{\partial^3 p}{\partial v^3}\right)_\theta}{\left(\frac{\partial p}{\partial v}\right)_\theta}(\Delta v)^2\right]. \tag{49}$$

Substitutions in (49) by means of (46), (47) and (48) give, neglecting terms with $\Delta v/v$ to the fourth and higher powers,

$$\Delta p_\theta = \left(\frac{\partial p}{\partial v}\right)_\theta \frac{\Delta v}{v}\left[1 - \beta\frac{\Delta v}{v} + \left(\frac{\Delta v}{v}\right)^2\right]v, \tag{50}$$

where

$$\beta = 1 + \frac{B}{A}\frac{\theta_c}{p_c}\frac{\alpha}{v} + \frac{3AC - 2B^2}{A^2}\frac{\theta_c^2}{p_c^2}\frac{\alpha^2}{v^2}, \tag{51}$$

in which α is the ratio of the two specific volume units, 1.00706. The term of (50) containing β is of the second order, consequently it is sufficient to have β approximately. Table X. gives such values to the nearest

TABLE X.

Values of β for equation (50).

P in Atmos	7.78	14.72	21.52	28.52	35.52	42.34	49.36	57.0
0° C.	.94	.88	.78	.66				
30	.96	.92	.87	.81	.74	.66	.55	.39
50	.97	.94	.90	.86	.82	.77	.71	.63
100	.98	.96	.95	.93	.91	.89	.87	.84

hundredth. Column 7, Table XI. contains the results of such computations for Δp_θ.

Calibrations and Miscellaneous Notes.—It should be noted here that various parts of the apparatus were carefully calibrated and measured. The differential surface tension effects in the manometer were always negligible. The changes in the density of the mercury due to the varying pressure were also found negligible. It was always to be noted on releasing the pressure in the apparatus that some CO_2 had been dissolved in the mercury. The amount was small, and, considering the limited amount of time at the writers' disposal, it never seemed sufficient to warrant an investigation. The possible effect of the dissolved CO_2 on the density of the mercury has been ignored. The pressure gauge was a Bowden steam test gauge of 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ range. It was carefully calibrated. In determining the pressure of the gas in the apparatus account was taken of the barometric pressure. Throughout the time of experimentation this was .97 atmo. The thermometers were compared with standard thermometers. The volume of the compression chamber was obtained by finding the weight of the water necessary to fill it. The

TABLE XI.

Data for and results on γ for CO_2. Preliminary Results.

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_ϱ in cm. of *Hg.*	Δp_θ in cm. of *Hg.*	γ	γ (corr.)	γ'	Purity of CO_2 in %.
July 22	29.4	14.72	C	3.004	13.10	9.77	1.342	1.340		99.2
25	32.7	7.78	C	3.004	7.04	5.37	1.310	1.311		99.6
27	32.4	14.72	C	3.004	13.24	9.79	1.352	1.350		
30	32.2	28.52	C	1.422	12.09	8.04	1.503	1.508		
Aug. 1	31.0	7.78	C	1.422	3.348	2.529	1.324	1.325		
3	31.4	7.78	C	1.422	3.337	2.528	1.320	1.320		
4	31.8	7.78	R	1.422	3.326	2.507	1.326	1.327		
5	31.7	7.78	C	2.122	4.94	3.48	1.306	1.306		
5	31.4	7.78	C	2.122	4.97	3.78	1.314	1.315		

TABLE XI.—*Continued.*

Data for and results on γ *for* CO_2. *Final Results.*

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_Q in cm. of *Hg.*	Δp_θ in cm. of *Hg.*	γ	γ (corr.)	γ'	Purity of CO_2 in %.
8	31.3	7.78	C	3.004	7.09	5.37	1.320	1.320	1.268	
9	30.8	7.78	R	3.004	7.01	5.32	1.317	1.317	69	
	31.5	14.72	R	3.004	13.20	9.71	1.359	1.360	63	
	32.2	14.72	R	1.422	6.18	4.60	1.344	1.346	50	
	31.7	14.72	C	1.422	6.23	4.61	1.352	1.353	51	99.6
10	31.2	28.52	C	1.428	12.05	8.09	1.488	1.489	50	
	31.8	28.52	R	1.428	12.14	8.06	1.505	1.509	63	
11	31.3	21.52	R	1.407	9.06	6.32	1.432	1.433	63	99.6
	31.2	21.52	C	1.407	9.09	6.34	1.434	1.434	62	
12	49.8	7.78	C	2.994	6.99	5.39	1.296	1.296	54	
	49.9	7.78	R	2.994	7.04	5.34	1.316	1.316	51	
	49.9	14.72	R	2.994	13.11	9.91	1.335	1.335	60	
	49.9	14.72	C	2.994	13.29	9.89	1.345	1.345	62	
	50.0	21.52	C	1.430	9.19	6.63	1.386	1.386	57	
	50.0	21.52	R	1.430	9.20	6.61	1.391	1.391	65	
13	50.0	28.52	C	1.421	12.15	8.39	1.448	1.448	61	
	50.1	28.52	R	1.421	12.10	8.37	1.447	1.447	64	
	50.2	34.52	R	.768	8.20	5.38	1.524	1.525	69	
	50.2	34.52	C	.768	8.16	5.39	1.515	1.516	62	
15	98.4	7.78	C	3.020	6.93	5.52	1.256	1.256	35	
	98.4	7.78	R	3.020	6.91	5.47	1.264	1.264	47	
	98.5	14.72	C	1.436	6.17	4.86	1.269	1.269	27	
	98.4	14.72	R	1.436	6.17	4.84	1.275	1.275	34	99.5
16	98.5	28.52	C	1.438	12.06	9.07	1.329	1.329	36	
	98.5	28.52	R	1.438	11.99	9.04	1.326	1.326	36	
	98.6	41.34	R	1.775	9.83	6.96	1.412	1.413	66	
	98.6	41.34	C	1.775	9.77	6.97	1.401	1.402	55	99.3
17	0.2	28.52	C	.786	6.49	3.83	1.694	1.694	48	
	0.2	28.52	C	1.425	11.91	6.95	1.710	1.710	34	
	0.2	28.52	R	1.425	11.81	6.94	1.702	1.702	32	
18	0.2	21.52	C	1.424	8.97	5.07	1.528	1.528	32	
	30.9	41.34	C	.786	9.93	5.61	1.771	1.770	59	
22	0.2	7.78	C	2.120	4.95	3.70	1.338	1.338	58	
	0.2	7.78	R	2.120	4.95	3.67	1.346	1.346	68	
23	98.6	34.52	C	.805	8.24	6.19	1.331	1.332	14	
	98.6	34.52	R	.805	8.27	6.18	1.339	1.340	24	
	98.6	48.36	C	.809	11.78	8.28	1.423	1.425	50	
24	31.6	7.78	C	4.388	10.31	7.88	1.309	1.309	57	
25	30.7	57.0	C	.798	13.78	5.85	2.36	2.35	82	
	31.1	7.78	C	3.038	7.12	5.43	1.310	1.310	58	

γ (corr.) indicates values of γ corrected to the standard temperatures 0°, 31°, 50° and 98.5° C.

volume of the chamber and its accessories is 310.0 cm^3. The average of 20 measurements of the diameter of the compressing piston gave 1.1098 cm. The purity of the gas was determined by bringing a known quantity of it into contact with KOH.

The time required for the thrusting in of the plunger H (Fig. 5) is a matter of some interest. If the thrusting in of the plunger and the reaching of a steady state by the gas could possibly occur in an extremely short interval such as .001 sec., one would need to give special consideration to the extremely high temperature gradient which would be established at the boundaries of the vessel. If, however, each of the two processes should take an appreciable time, no very high temperature gradient is to be expected at any instant. The time of inthrust of the plunger H was determined by taking the difference between two selected intervals. The first interval was from the starting of the plunger H to the opening of stop-cock S_3, the interval being recorded in the manner described above by the chronoscope. The second interval differed from the first in that the contact beginning the interval was made near the end of the inthrust instead of at the beginning. The average of several such determinations showed that the time for the maximum inthrust was about .06 sec. In the measurements made this interval of inthrust was always included. Of course, for the smaller inthrusts, this interval was smaller.

Data and Results.—The data taken and the values of γ obtained are shown in Table XI. The values given may in a few cases differ by .001 from the quotient of Δp_Q by Δp_θ because of the manner in which the former were obtained. The corrections for obtaining γ (corr.) for the four standard temperatures were obtained from an initial rough plat. The computed values of γ for these four standard temperatures have been platted in Fig. 9 as a function of the pressure. With a few exceptions, each platted point represents the mean of two determinations of γ, one from a compression, the other from a rarefaction. Two pairs of such values have been included in the point for the gas at 31° C. and a pressure of 7.78 atmospheres. The higher values were obtained early in the work. The lower values were obtained near the end. Sometime between August 18 and August 23, the date unfortunately not being recorded, the rubber washer between the compression chamber and its lid was replaced by a new one, which was noticeably thicker than the one removed. The importance of the consequent change in the volume of the compression chamber was not appreciated fully at the time or accurate measurements would have been taken. Account has not been taken of this change in the computations. However, if account should be taken of this change of volume, the separately determined values would more nearly coincide. The same is to be said regarding the values for γ at 98.5° C. for pressures of 35.52 atmospheres and 49.36 atmospheres. In this instance the values of γ taking account of the volume change

would also be raised so that the variations of the platted γ for this temperature would be less noticeable. The same possibility applies to γ for 0.2° C. at 7.78 atmospheres. It is to be noted that the preliminary values of γ, though not platted, agree very well with the final results.

Result of Maneuvrier and Results Based on C_v by Joly.—There is platted for comparison purposes the value of 1.298 determined by Maneuvrier,[37] the originator of this method, for CO_2 at atmospheric pressure and 10° C. Values of γ for CO_2 at atmospheric pressure have been rather discordant. Generally, however, such values approximate the results obtained here,

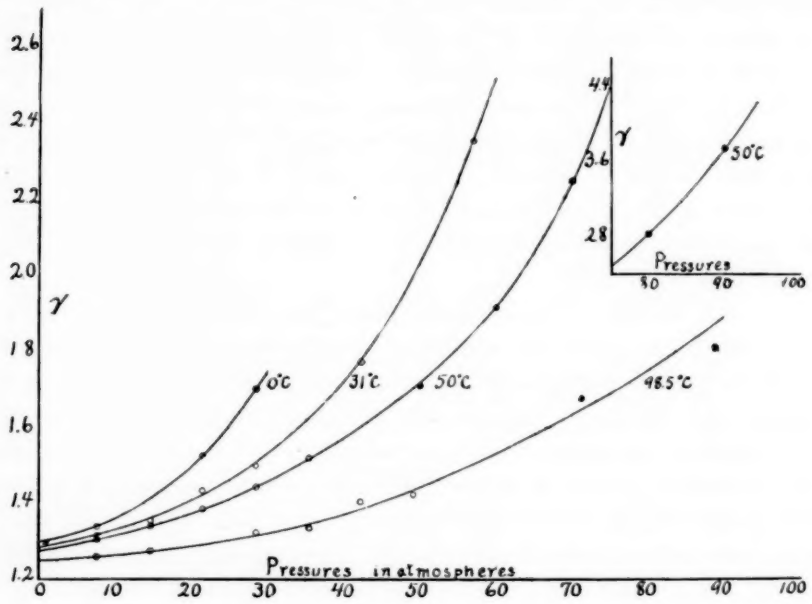

Fig. 9.

Variation of γ in CO_2 with pressure and temperature.

Results based on determinations
of C_v by Joly ..... ●
of Δp_a by Worthing ..... ○
of Maneuvrier ..... +

though the variation with temperature has been found to be less noticeable than what the writer has obtained. There are also platted values of γ which are based on determinations of C_v by Joly. The method of computing was that used by Amagat.[31] Values of C_v and p, v, θ relations from the experimental data of Amagat were combined according to (13). This has been done by Amagat. The writer has not been able to verify fully the computations of Amagat and has here incorporated results from his own computations. The writer in determining $(\partial p/\partial\theta)_v$ and $(\partial v/\partial\theta)_p$

has used a graphical method. The values determined represent true values for the temperatures and pressures indicated. The values of C_v for pressures of 80 and 90 atmospheres at 50° C. have been taken from Amagat's extrapolation. The values for C_v at 100° C. result directly from equations given by Joly for CO_2 at densities .1240 gr./cm.^{3} and .1800 gr./cm.^{3} Table XII. includes these data and results. The general agreement is quite satisfying.

TABLE XII.

Data for and results on γ for CO_2 based on C_v determinations by Joly and p, v, θ determinations by Amagat.

T	p	C_v	$C_v\left(\frac{\partial v}{\partial \theta}\right)_p$	$-\left(\frac{\partial p}{\partial v}\right)_\theta$	C_p	γ
50°C.	50	.1920	.0$_3$1310	2020	.329	1.710
	60	.2015	1280	2850	.386	1.915
	70	.2108	1345	3670	.474	2.245
	80	.2303	1530	4560	.644	2.83
	90	.2585	1800	5500	.945	3.73
100	71.3	.1902	0870	3690	.318	1.670
	87.8	.2056	0805	5590	.372	1.810

p is expressed in atmospheres, C_p and C_v in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$.

γ' of Equation $pv^{\gamma'} = constant$.—In the column (Table XI.) headed γ' are included values which are derived on the assumption that for the processes of compression and rarefaction considered, there holds the following relation:

(52) $$pv^{\gamma'} = \text{constant}.$$

The approximate constancy of γ' for a given temperature is remarkable and is worthy of further experimental consideration. A γ', of course, is not to be interpreted as a ratio of the two heat capacities except perhaps for the gas under zero pressure at the same temperature, or as described by the same adiabat, or under some other similar conditions. Differentiation of (52) and the application of (43) give

(53) $$\left(\frac{\partial p}{\partial v}\right)_Q = -\gamma' \frac{p}{v} = \gamma \left(\frac{\partial p}{\partial v}\right)_\theta.$$

Whence

(54) $$\gamma = -\gamma' \frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_\theta,$$

or according to Bakker[30]

(55) $$\frac{\gamma - \gamma'}{\gamma'} = -\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_\theta - 1 = \text{departure of gas from Boyle's law.}$$

Extrapolation to zero presssure, making use of these values of γ', would seem to indicate that the platted curves of γ (Fig. 9), on being extrapolated back to zero pressure, had been extrapolated to too high values of γ. Not a great deal of dependence may be placed on this, however, until more is known about the function γ'.

Conclusions regarding γ *and* γ'.—The plats and tables show for CO_2 for the region considered:

1. The ratio of the two heat capacities γ for a given pressure decreases with an increase of temperature.

2. γ for a given temperature increases with pressure.

3. The curve for γ at 30° C. is such as to be consistent with the theoretical infinite value of γ at the critical point.

4. The agreement of the values based on Δp_Q data with those based on C_v data by Joly is very good.

5. The results at atmospheric pressure are in fair agreement with the results of others.

6. γ', where $pv^{\gamma'}$ = constant applies to reversible adiabatic changes, is approximately constant.

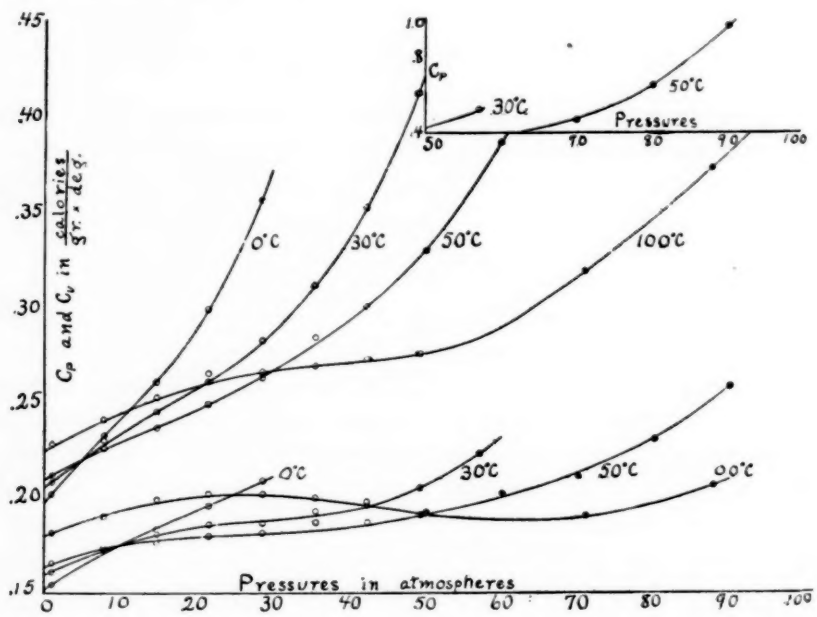

Fig. 10.

Variation of C_p and C_v of CO_2 with pressure and temperature.

Results based on determinations

of C_v by Joly ..... ●

of γ by Worthing ..... ○

V. Determination of C_v and C_p for CO_2.

Determinations from the Present Work.—Equation (13) gives at once

$$(56) \qquad (\gamma - 1)C_v = \theta\left(\frac{\partial p}{\partial \theta}\right)_v\left(\frac{\partial v}{\partial \theta}\right)_p.$$

This enables one to determine C_v and hence C_p by means of the data already obtained. The method of computation is evident. The transformation factor used in this work in the changing of the units of C_v and C_p to the ordinary units is expressed in (57).

$$(57) \qquad 1\,\frac{\text{atmos.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}} = 12.24\,\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}.$$

Values of C_v and C_p are to be found in Table XIII. Values of $(\partial p/\partial\theta)_v$, $(\partial v/\partial\theta)_p$ and $\theta(\partial p/\partial\theta)_v(\partial v/\partial\theta)_p$ are included in the hope that they may save some one otherwise extended computations. In Fig. 10 C_v and

TABLE XIII.

Data for and results on C_p and C_v of CO_2.

T	p	γ	$\log\left(\frac{\partial p}{\partial\theta}\right)_v$	$\log\left(\frac{\partial v}{\partial\theta}\right)_p$	$\log\left[\theta\left(\frac{\partial p}{\partial\theta}\right)_v\left(\frac{\partial v}{\partial\theta}\right)_p\right]$	C_v	C_p
0	7.78	1.342	$\bar{2}$.5130	$\bar{4}$.7359	$\bar{3}$.6852	.173	.233
	14.72	1.418	.8459	.5156	.8856	.184	.261
	21.52	1.528	$\bar{1}$.0707	.4206	.9276	.196	.299
	28.52	1.702	.2630	.3796	$\bar{2}$.0789	.209	.356
30	7.78	1.314	$\bar{2}$.4501	.7169	$\bar{3}$.6486	.174	.230
	14.72	1.360	.7652	.4770	.7238	.180	.245
	21.52	1.420	.9680	.3545	.8041	.186	.265
	28.52	1.509	$\bar{1}$.1315	.2778	.8909	.187	.282
	35.52	1.621	.2727	.2362	.9905	.193	.311
	42.34	1.779	.3978	.2203	$\bar{2}$.0997	.198	.353
	49.36	2.01	.5200	.2271	.2287	.205	.412
	57.0	2.37	.6540	.2602	.3958	.223	.528
50	7.78	1.304	$\bar{2}$.4143	.7092	$\bar{3}$.6328	.173	.226
	14.72	1.340	.7208	.4620	.6921	.177	.237
	21.52	1.386	.9159	.3291	.7543	.180	.249
	28.52	1.447	$\bar{3}$.0709	.2414	.8216	.182	.263
	35.52	1.521	.1997	.1826	.8916	.187	.284
	42.34	1.603	.3100	.1441	.7964	.187	.300
100	7.78	1.260	$\bar{2}$.3401	.6966	.6085	.191	.241
	14.72	1.272	.6359	.4376	.6453	.199	.253
	21.52	1.291	.8188	.2920	.6826	.202	.261
	28.52	1.319	.9602	.1887	.7207	.202	.266
	35.52	1.353	$\bar{1}$.0750	.1127	.7595	.199	.269
	42.34	1.392	.1699	.0551	.7968	.196	.273
	49.36	1.44	.2561	.0089	.8368	.191	.275

p is expressed in atmopsheres, v in $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$ and C_v and C_p in $\frac{\text{calories}}{\text{gr.} \times \text{degree}}$.

C_p are platted as functions of p. Values based on Joly's measurements (Table XII.) are included.

C_p Agreement with the Results of Others.—Very little agreement is to be found between the values of C_p here computed and the values of C_p obtained from a plat of Lussana's[33] results. The values of C_p for a pressure of one atmosphere as determined by the direct experiments of Holborn and Austin[42] and by those of Swann[43] and as computed here are included in Table XIV. Excepting for the 100° C. value, the computed results agree very well with the results of Holborn and Austin. At 100° C. the agreement is not good, though a better agreement is to be found with Swann's value for this temperature.

TABLE XIV.

Values of C_p for CO_2 at atmospheric pressure expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

T	Holborn & Austin	Swann.	Worthing.
0	.203		.202
20		.202	
30	.207		.208
50	.210		.212
100	.216	.221	.228

Causes for Possible Experimental Error.—Realizing early that the values for γ at 100° C. were slightly lower than was expected, special care was taken with the measurements. It is also, of course, an open question whether or not Kammerlingh Onnes's equation, which here bridges an experimental gap from 1 to 50 atmospheres and which here reaches its upper temperature limit of application, correctly represents the interrelations of p, v and θ for this region. The writer can not see how any experimental error in his work might produce this discrepancy. The supposition that the gas in the compression chamber has not all reached the temperature of the bath would lead to a discrepancy in the opposite direction, as would also the fact that a small amount of the gas, that in a portion of the connecting tubes, is at a considerably lower temperature than the bath. The possibility of local cooling next to the plunger during a compression might be thought to explain a part of the discrepancy. But that this is of small consequence is indicated by the good agreement obtained for γ by the rarefaction and by the compression measurements (Table XI.). Moreover, any such experimental error would be effective at the higher pressures, tending to produce too high values for C_v as well as C_p, an effect which is not in evidence in comparing the present results with Joly's (Figs. 9 and 10).

C_v Comparison with Joly's Results.—The attempt to compare the results on C_v computed above with the direct experimental values of Joly[32] has not been as thorough as might be wished due to insufficient data. Joly concluded that the variations of C_v with temperature were very small for densities less than .08 gr./cm.^{3} for the temperature interval 0° C. to 100° C. The fact that his data do not strictly bear out his conclusion was ascribed to the observational inaccuracies entering in his work at the lower densities. This conclusion was accepted in the forming of Table VI. If it is fully accepted, very little agreement is to be found between the writer's values of C_v and those of Joly's. Moreover, it is not compatible with the results of Holborn and Austin and of Swann on C_p at one atmosphere and the ordinarily accepted variations of γ with the temperature for the same pressure. These would require that at atmospheric pressure C_v should increase noticeably with temperature, a variation just the opposite of that found by Joly for the higher pressures. The writer has assumed that the apparent disappearance of a temperature effect with decreasing densities in Joly's results might have been a disappearance preparatory to a reversal of the temperature effect, and has computed from Joly's individual results what the values of C_v would be for certain densities and temperatures if the results were correct. In doing this Joly's equation for C_v at a density of .124 gr./cm.^{3} has been used. For the densities .0800 gr./cm.^{3} and .0456 gr./cm.^{3} values of C_v were obtained by the deriving of an equation holding over a portion of the temperature range in a manner similar to that used by Joly. Other values of C_v were obtained by a quadrature method based on the general principle that

$$C_v = \frac{\partial}{\partial T}\left[\overline{C}_v(100 - T)\right]_v, \tag{58}$$

where $\overline{C}_v$ is the mean value of C_v between T and 100° C. These results with corresponding values obtained from the writer's work are included in Table XV. The table indicates a fair agreement between the results

TABLE XV.

Corresponding values of C_v as determined by Joly and by Worthing.

T	p	C_v (Joly.)	C_v (W.)	p	C_v (Joly.)	C_v W.)	p	C_v (Joly.)	C_v (W.)
0°	19.4	.194	.193						
30	22.6	.178	.186	36.0	.189	.193	49.0	.208	.205
50	24.6	.170	.181	40.0	.185	.186			
100	29.5	.206	.202	49.0	.200	.192			

p is expressed in atmospheres, C_v in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of Joly thus interpreted and the writer's. As suggested above, insufficient data may account for a part of the actual variations.

Conclusions Regarding C_v and C_p.—For the region considered in CO_2, the following conclusions may be drawn:

1. The isometric heat capacity of CO_2, C_v, at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.

2. For a given temperature C_v generally increases with increasing pressure. The reverse is true for a certain pressure interval at 100° C.

3. There is a good agreement between the results on C_v obtained by the writer and those obtained by Joly.

4. The isopiestic heat capacity C_p at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.

5. For a given temperature C_p increases with increasing pressure.

6. The variation of C_p at 30° C. is such as to be consistent with a theoretically infinite value at the critical point.

7. At atmospheric pressure the computed values of C_p agree well with the experimental values of Holborn and Austin and of Swann.

8. At high pressures the values found using the writer's experimental results are such as to be consistent with results based on Joly's data on C_v.

9. Very little agreement has been found between the writer's results and Lussana's results.

VI. The Free-Expansion and Joule-Kelvin Effects in CO_2.

Results.—The methods of computation were those detailed in connection with the free-expansion and Joule-Kelvin effects in air. The results are to be found in Table XVI. Results for pressures of 50 atmospheres and higher for 50° C. and 100° C. have been determined by taking the results of Joly on C_v, the individual values being taken from the curves of Fig. 10. A value for both μ and η at the critical point (p = 72.9 atmos., θ = 304.5° K.) has been obtained by Keesom[44] by measuring the $dp/d\theta$ of the vapor tension curve of CO_2 at that point. Theoretically at the critical point of a substance there exists but a single value for $dp/d\theta$. This follows at once from (8), since at this point $(\partial p/\partial v)_\theta = 0$. Consequently we have

$$\mu_c = \eta_c = \left(\frac{d\theta}{dp}\right)_c \tag{59}$$

where the subscript c indicates the critical point values. These values of μ and η are included in Table XVI. The results as functions of the

TABLE XVI.

Data for and results on μ and η for CO_2. Results based on K. Onnes's equation and on γ data by Worthing.

T in °C.	p in Atmos.	$\theta - v\left(\frac{\partial\theta}{\partial v}\right)_p$ in °K.	$\theta\left(\frac{\partial p}{\partial\theta}\right)_v - p$ in Atmos.	μ in deg./atmo.	η in deg./atmo.	$\frac{\Delta W_1}{\Delta W_2}$
0	7.78	48.8	1.12	1.398	1.266	.144
	14.72	87.9	4.44	1.333	1.259	.302
	21.52	125.9	10.62	1.334	1.262	.494
	28.52	161.3	21.52	1.329	1.265	.750
30	7.78	38.3	.76	1.084	.979	.098
	14.72	69.5	2.93	1.051	.978	.199
	21.52	99.7	6.64	1.063	.989	.309
	28.52	128.3	12.51	1.054	.993	.440
	35.52	157.0	21.28	1.059	1.008	.600
	42.34	183.6	33.42	1.061	1.023	.790
	49.36	209.4	51.04	1.048	1.023	1.035
	57.0	235.2	79.67	.995	.985	1.40
50	7.78	33.3	.61	.926	.833	.078
	14.72	60.3	2.27	.901	.827	.154
	21.52	86.5	5.10	.905	.836	.237
	28.52	112.4	9.52	.912	.854	.334
	35.52	136.5	15.65	.914	.868	.440
	42.34	158.8	23.62	.905	.870	.560
100	7.78	24.3	.38	.618	.557	.049
	14.72	44.3	1.41	.587	.537	.096
	21.52	63.9	3.06	.586	.530	.142
	28.52	82.5	5.52	.586	.539	.194
	35.52	100.4	8.82	.591	.553	.249
	42.34	116.7	12.84	.596	.565	.304
	49.36	133.1	17.96	.604	.583	.364
Results Based on C_v Data by Joly and p, v, θ Data by Amagat.						
50	50	183	35.6	.895	.865	.713
	60	212	58.0	.860	.850	.980
	70	240	89.8	.835	.835	1.28
	80	265	145.5	.765	.780	1.82
	90	286	230.0	.655	.670	2.62
100	71.3	190	48.4	.635	.660	.68
	87.8	221	80.2	.585	.615	.92
Results Based on $dp/d\theta$ at Critical Point by Keesom.						
31	72.9	304	416.	.622	.622	5.71

closely to the drawn curves. The variations here are such as would indicate that for good agreement of the results among themselves, the values of γ for the lower pressures should be somewhat less than they have been indicated to be. This is in exact conformity with the indications derived above in considering γ' of (49). However, the smallness

pressure and the temperature are platted in Fig. 11. Excepting for the values at zero pressure and at 7.78 atmospheres, the points lie very of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$ for low pressures might well account for the variations in μ and η in such cases.

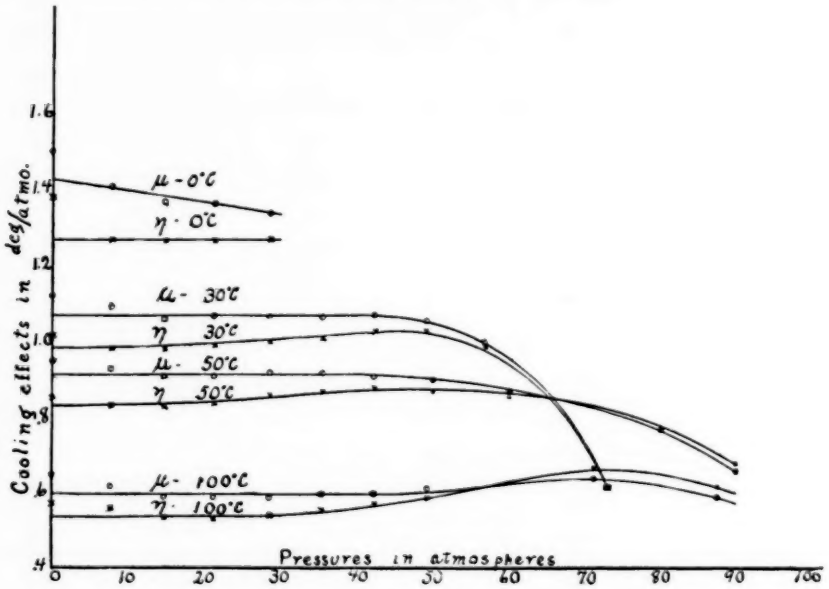

Fig. 11.

Variation of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 with temperature and pressure.

Results based on determinations of

C_v by Joly ..... ● ■

γ by Worthing ..... ○ ×

$\frac{dp}{d\theta}$ by Keesom ..... ■

Results for Low Pressures.—In Fig. 12 there have been platted μ and η as functions of the temperature for the gas under low pressures. There have been indicated also the results of Kester,[14] Joule and Kelvin,[9] Natanson[13] and some other observers. The non-agreement of μ and η at zero pressures with values at the higher pressures led the writer to consider the application of data by Chappuis[45] on the p, v and θ interrelations and data on C_p by Holborn and Austin. Chappuis's results are expressed in equations of the form

$$pv = A + Bp \tag{60}$$

for five different temperatures, − 17.5°, 0°, 20°, 40° and 100° C. A and B are constants. The unit of pressure used is that due to a meter

column of mercury, the unit of volume is that occupied by a gram molecule of the gas, at 0° C., under a pressure equal to that due to a meter column of mercury. In a method exactly analogous to that used in obtaining (27) and (28), we get for $p = 0$

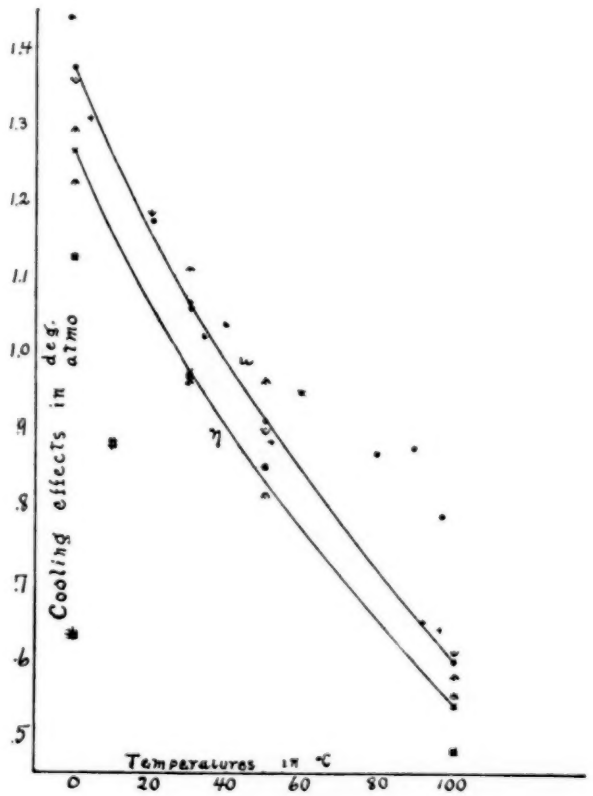

Fig. 12.

Variation with temperature of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 at low pressures.

Determinations of Joule-Kelvin effects

by Joule and Kelvin ..... +
by Natanson ..... ⩛
by Kester ..... ●
from data by Chappuis and by Holborn and Austin ..... ⩓
from Clausius's equation ..... ⊍
by Worthing ..... ○

Determinations of free-expansion effects

by Cazin ..... #
by Searle ..... *
from data by Chappuis and by Holborn and Austin ..... ⊡
from Clausius's equation ..... ⊙
by Worthing ..... ×

$$\mu_0 = \frac{\theta\left(\frac{\partial B}{\partial \theta}\right)_p - B}{C_p}, \tag{61}$$

$$\eta_0 = \frac{\theta\left(\frac{\partial B}{\partial \theta}\right)_p}{C_p - \frac{A_0}{\theta_0}}, \tag{62}$$

where A_0 and θ_0 are the values of A and θ for 0° C. (61) and (62) are based on the assumption that

$$A = A_0 \frac{\theta}{\theta_0}, \tag{63}$$

a condition which is necessary if the gas in question is to approach the condition of a perfect gas as the pressure approaches zero. Chappuis's constants do not quite fulfil condition (63). Slight changes were made in his values for A and B, leaving the values for A and B at 0° C. and the values of pv at the unit of pressure unchanged, such that condition (63) was fulfilled. This seems reasonable, in view of the added fact that, of the measurements by Chappuis at three different pressures, the average pressure was about equivalent to that due to a meter column of mercury. Thus changed B is readily and with a great deal of accuracy expressed by the following empirical formula,

$$10^5 B = -906 + 6.87T = .0226T^2. \tag{64}$$

Chappuis's value for A_0 is 1.00906. The values indicated as being based on data by Chappuis and by Holborn and Austin, were obtained under the above named conditions. Some check computations for μ and η at 1 m. of Hg pressure based on quadrature methods and using Chappuis's constants unchanged showed excellent agreement with the values obtained using the modified constants of (63) and (64). To obtain values of C_p at zero pressure Holborn and Austin's data were used in conjunction with the change for one atmosphere indicated by the curves in Fig. 10. The results indicated as being based on Clausius's equation were obtained for zero pressure by a method analogous to that used in obtaining (27), and (28), and (61) and (62). Clausius's[46] equation and the numerical values of the constants are given in (65).

$$p = \frac{R\theta}{v - a} - \frac{c}{\theta(v + b)^2} \tag{65}$$

$$R = .003688,$$
$$a = .000843,$$
$$b = .000977,$$
$$c = 2.0935.$$

The resulting values for μ and η at zero pressure are

$$\mu_0 = \frac{\gamma - 1}{\gamma}\left(\frac{3c}{R^2\theta^2} - \frac{a}{R}\right), \tag{66}$$

$$\eta_0 = \frac{2c(\gamma - 1)}{R^2\theta^2}. \tag{67}$$

The curves of Fig. 9 furnished the desired values of γ. The value found by Searle[8] was obtained through considering the application of Van der Waal's equation. The value by Cazin[7] is an average of the four values .81, .82, .82 and 1.09 deg./atmo. which are obtainable from his results. The method is briefly described in the introduction. The first value is directly obtainable from his results. The other values are obtained indirectly. In obtaining his results for these three cases, Cazin had the larger chamber, into which the gas experimented on expanded from a smaller chamber, partially filled with the gas. In arriving at the above values, the rough assumption was made that the gas freely expanding was that in the smaller chamber in excess of the amount necessary to produce it in a pressure equal to the pressure existing in the larger chamber.

Note Regarding Disagreement of Values at Zero Pressure.—The high values of μ and η for $p = 0$ using Kammerlingh Onnes's equation (Fig. 12), are offset by the results based on the careful work of Chappuis and the work of Holborn and Austin and the results obtained with the aid of Clausius's equation. The difference arises from small variations in the p, v, θ relations. This disagreement might seem to cast doubt upon the values for the higher pressures. This is not necessarily the case, however, for with increasing pressure, as mentioned before, small errors in the p, v, θ relation become less effective due to the relative increase in size of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$.

Internal Work during Expansion.—As in the case with air, it is of interest to consider the relative magnitude of the internal work on expansion when compared with the external work. (35) gives this relation for an infinitesimal, reversible, isothermal expansion. Values of $\frac{\Delta w_1}{\Delta w_2}$ are included in the final columns of Table XVI. The results, excepting the value 5.71 for the critical point, have been platted in Fig. 13. The platted points fall very closely on the smoothed curves. The effects of temperature and pressure are well shown. This plat incidentally shows very plainly the cause for the h'gh values for γ at the higher pressures. In determining the isopiestic heat capacity of a gas, one neces-

sarily must consider the internal work of expansion, a factor which does not enter into the isometric heat capacity. Consequently there are relatively large values of γ, where the values of $\frac{\Delta w_1}{\Delta w_2}$ are relatively large. This relation is further borne outby the striking si milarity of the two plats.

Conclusions Regarding and μ, η, $\frac{\Delta w_1}{\Delta w_2}$ *for* CO_2.—The following conclu-

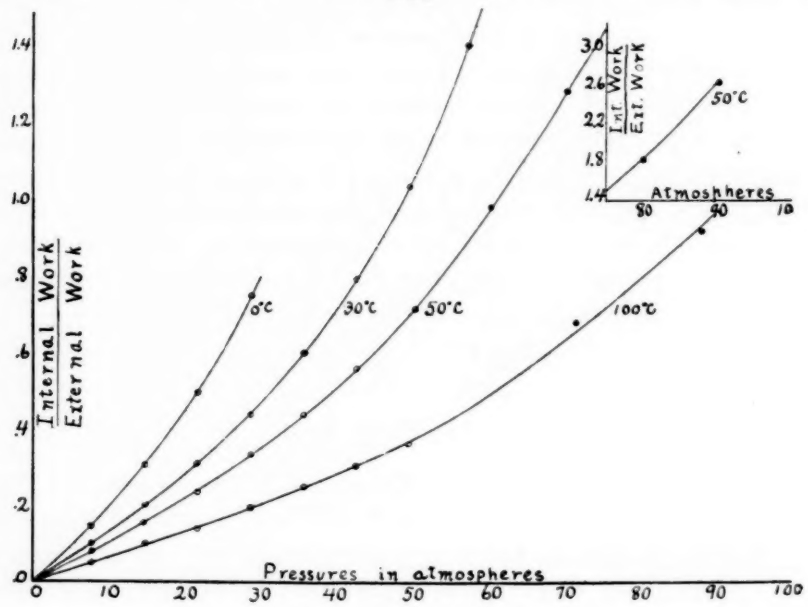

Fig. 13.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ for reversible, infinitesimal, isothermal expansions in CO_2.

Results based on determinations of

C_v by Joly ..... ●

γ by Worthing ..... ○

sions for CO_2 for the regions considered may be drawn from the plats of μ, η and $\frac{\Delta w_1}{\Delta w_2}$.

1. For pressures up to about 60 or 70 atmospheres the free-expansion effect is less everywhere than the corresponding Joule-Kelvin effect. For the higher pressures the reverse is true.

2. For pressures up to about 60 or 70 atmospheres the values of μ and η decrease with increasing temperatures for the temperature interval 0° to 100° C. For sufficiently high pressures there is a reversal of this temperature effect.

3. μ for a given temperature is approximately independent of the pressure up to about 40 atmospheres. For higher pressures (excepting at 100° C.) it decreases with increasing pressure.

4. η for a given temperature is nearly constant with varying pressure up to about 30 atmospheres. With increasing pressures η first increases slightly, then decreases more rapidly.

5. There is general good agreement among the μ and η determinations based on the different experimental data.

6. The writer's computed values for μ at moderate pressures agree very well with the experimental values of Joule and Kelvin and with the values obtained by using Clausius's equation, but are consistently less than the results of Kester.

7. The writer's values for η show excellent agreement with the values to be computed on making use of Clausius's equation.

8. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ is greater for a given pressure the lower the temperature.

9. The ratio $\frac{\Delta w_1}{\Delta w_2}$ starts with zero values at zero pressure and increases with pressure, reaching a value of 5.71 at the critical point.

VII. Significance of a Noticeable Relation between μ and η for Air and for CO_2.

It is to be noticed that the results for μ and η for air and CO_2 show some marked differences. Among them is the fact that η is greater than μ in air for the region considered, while the reverse is true for a large portion of the region considered in the case of CO_2. A brief discussion of this fact may perhaps bring out the significance of this. Consider Fig. 14 in which POQ represents an isothermal platted on a (pv, p) diagram. Consider some gas to be in a state represented by O on the diagram and about to be expanded through a porous plug. On the diagram, the path representing the change will evidently proceed from O to some point to the left of mn,

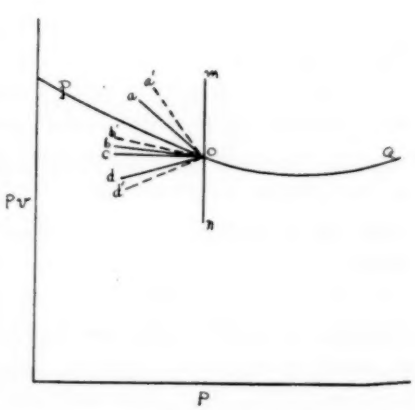

Fig. 14.

an isopiestic through O. In case the path should be along Ob, Oc or Od, cooling of the gas would occur and a positive Joule-Kelvin effect, as in air or in CO_2, would be evidence. In case the path should be along Oa, heating of the gas would occur and a negative Joule-Kelvin effect as in hydrogen would be evidenced. The condition necessarily fulfilled in a porous plug expansion is

$$\Delta\epsilon + \Delta(pv) = 0. \tag{68}$$

The condition necessarily fulfilled in a free-expansion is

$$\Delta\epsilon = 0. \tag{69}$$

According to conditions, for instance whether in Fig. 14 the path proceeds from O into the upper left hand quadrant, along Oc, or into the lower left hand quadrant, we have respectively for the porous plug expansions

$$\Delta(pv) > 0, \quad \Delta(pv) = 0, \quad \Delta(pv) < 0. \tag{70}$$

For these cases we also have respectively

$$\Delta\epsilon < 0, \quad \Delta\epsilon = 0, \quad \Delta\epsilon > 0. \tag{71}$$

In the first case, where the path representing the porous plug expansion proceeds into the upper left hand quadrant and for which $\Delta\epsilon < 0$, the path for a free-expansion, in which $\Delta\epsilon = 0$, lies above that for the porous plug expansion. Hence, taking into account the signs of the effects, the free-expansion effect is less than the Joule-Kelvin effect.

In the second case, where the path representing the porous plug expansion proceeds along Oc and where $\Delta\epsilon = 0$, the path for a free-expansion also proceeds along Oc. Here the two cooling effects are equal.

In the third case, where the path representing the porous plug expansion proceeds from O into the lower left hand quadrant and for which $\Delta\epsilon > 0$, the path for a free-expansion in which $\Delta\epsilon = 0$, lies below that for the porous plug expansion. Here the free-expansion effect is greater than the porous plug effect. The converse of these statements is also true.

In the regions considered in air and in CO_2 we have for the most part portions of isothermals which when represented on diagrams as in Fig. 14 correspond to the portion PO. In air where the Joule-Kelvin and free-expansion effects are both positive and the latter the greater, we have porous plug expansions and free-expansions whose paths would correspond respectively to Od and Od'. For CO_2 at the lower pressures, where the Joule-Kelvin and free-expansion effects are both positive and

the latter the smaller, the corresponding paths are *Ob* and *Ob'*. At somewhat higher pressures where the two effects are equal, the corresponding paths coincide and lie along *Oc*. At still higher pressures where the two effects are reversed, we have conditions existing as described above in air.

VIII. Summary.

1. An expression has been developed which shows clearly the relation between the free-expansion effect η and the ratio of the two heat capacities γ of a substance.

2. With the aid of γ data by Koch, $pv\theta$ data by Witkowski and an empirical equation of state by Kammerlingh Onnes, there have been computed values for the free-expansion effect η, the Joule-Kelvin effect μ and the ratio of the internal work to the external work for infinitesimal reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ for air at 0° C. and at − 79.3° C. and for pressures up to 130 atmospheres.

3. With the aid of Kammerlingh Onnes's equation of state, there have been obtained experimentally by Maneuvrier's method values of γ for CO_2 at 0.0°, 31.0°, 50.0° and 98.5° C. and for pressures ranging from about 8 atmospheres to 57 atmospheres.

4. The approximate constancy of a new function γ' where γ' is defined by $pv^{\gamma'} = \text{constant}$—for CO_2 has been pointed out.

5. Values for the isometric heat capacity C_v, the isopiestic heat capacity C_p, μ, η and $\frac{\Delta w_1}{\Delta w_2}$ for CO_2 at 0°, 30°, 50° and 100° C. and for pressures—making use of C_v data by Joly—up to 90 atmospheres have been computed.

6. The results of the present work have been shown to be generally in good agreement with the experimental results of others.

7. A discussion has been presented in which certain characteristics of the expansions of air and of carbon dioxide through a porous plug and into a vacuum are considered.

The conclusions reached regarding the variations of the various quantities considered will be found summarized at the close of the different subdivisions of the present paper.

In conclusion, I wish to express my sincere thanks to Mr. R. E. Miller for care shown in the construction of the apparatus, to Mr. C. E. Guthe, Jr., for efficient aid given in the experimental work, and especially to Dr. K. E. Guthe for his kindly interest and helpful suggestions.

University of Michigan,
Ann Arbor, Mich.,
March, 1911.

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THE MAGNETIZATION OF COBALT AS A FUNCTION OF THE TEMPERATURE AND THE DETERMINATION OF ITS INTRINSIC MAGNETIC FIELD.

BY W. W. STIFLER.

INTRODUCTION.

THOUGH cobalt has always been classed as one of the strongly magnetic metals, its properties do not seem to have been studied with the interest manifested in those of iron and nickel. In spite of the work of E. Becquerel,[1] Plücker,[2] Rowland,[3] Hankel,[4] H. Becquerel,[5] Gaiffe,[6] Trowbridge and McRea,[7] Berson,[8] Bidwell,[9] Ewing and Low,[10] duBois,[11] Fleming, Ashton and Tomlinson,[12] Beattie,[13], and Nagaoka and Honda,[14] until very recently the amount of real numerical data on the magnetic properties of cobalt, even at ordinary temperatures, was very meagre.

Within the last two years several articles have been published which are of great interest from a theoretical point of view. One of these is by P. Weiss[15] and gives the results of work at ordinary temperatures; another is by Weiss and Kamerlingh Onnes[16] and gives the results of their work at very low temperatures. In the investigation described in the first of these papers, the saturation value of the specific intensity of

[1] Comp. Rend., *20*, pp. 1708–1711, 1845.

[2] Pogg. Ann., *91*, pp. 1–56, 1854.

[3] Phil. Mag., *164*, pp. 321–340, 1874.

[4] Ann. der Physik, N. F. *1*, pp. 285–296, 1877.

[5] Ann. de Chim. et de Phys., Ser. 5, *16*, pp. 227–286, 1879; Comp. Rend., *88*, pp. 111–114, 1879.

[6] Comp. Rend., *93*, pp. 461–462, 1881.

[7] Proc. Am. Acad. Arts and Sciences, *20*, pp. 462–472, 1884–85.

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[12] Phil. Mag., *214*, pp. 271–279, 1899.

[13] Phil. Mag., *217*, pp. 642–647, 1901.

[14] Phil. Mag., *220*, pp. 45–72, 1902.

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magnetization—that is, the intensity of magnetization per gram—was determined. Weiss found that the law of approach to saturation at 17° C. for cobalt was given by the equation

$$\sigma = 162\ (1 - 1.11\ \frac{10^6}{H^2}),$$

where σ is the specific intensity of magnetization. By plotting σ as a function of $1/H^2$ and extrapolating he found the saturation value to be 162 at 17° C. These results were confirmed by the work of Droz[1] published at the same time. In the second investigation measurements were taken at temperatures as low as that of liquid hydrogen. The value of σ at these very low temperatures was found to be less than 163.6.

Very recently Weiss[2] has measured the specific susceptibility of cobalt in the temperature interval from 1156° C. to 1302° C. using a method similar to that employed by Curie in his classical researches on the magnetic properties of bodies at high temperatures.[3] This article was published some months after the present investigation was undertaken. Weiss states that the "Curie point" for cobalt is probably in the neighborhood of 1110° C.

The recent developments of the electron theory of magnetism make a knowledge of the saturation value of the intensity of magnetization as a function of the temperature of great theoretical interest and the present investigation was undertaken with the objects:

1. To determine the specific intensity of magnetization at various temperatures up to about 1150° C.; that is, to a temperature somewhat above that at which spontaneous ferro-magnetism disappears.

2. To deduce from these data the value of the intrinsic molecular field of cobalt and the moment of its elementary magnet.

METHOD.

For this purpose, the method used by Weiss[4] seemed best adapted. It consists essentially in observing the throw of a ballistic galvanometer connected in series with a helix placed in a strong longitudinal magnetic field when an ellipsoid of the substance to be tested is suddenly jerked out of the helix. The throw of the galvanometer is then compared with that produced when a known current is made or broken through the primary of a standard helix, the secondary of which is included in the galvanom-

[1] Archives des Sciences (Geneve), Ser. 4, *29*, pp. 204–224 and 290–309, 1910.

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eter circuit. The connections are shown diagrammatically in Fig. 1, where C is the cobalt ellipsoid; H is the induction helix connected in series with the controlling resistance, R', the galvanometer, G, and the secondary, S, of the standard helix; P is the primary of the standard helix; R, the controlling resistance; and A is a carefully calibrated ammeter.

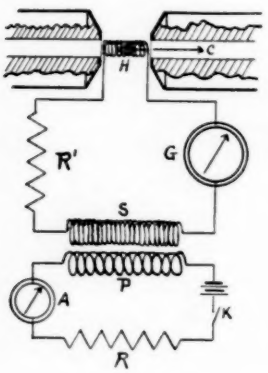

Fig. 1.

The formulæ for σ and I by this method are easily shown to be

$$\sigma = \frac{n_1 n' A (1 - d_1^2/2l_1^2)}{10mn(1 - d_2^2/2l_2^2)} \cdot \frac{I'}{d'} \cdot d = K \cdot d,$$

and

$$I = \frac{n_1 n' A (1 - d_1^2/2l_1^2)}{10Vn(1 - d_2^2/2l_2^2)} \cdot \frac{I'}{d'} \cdot d = K' d.$$

where A = area of cross section of primary of standard helix.
n_1 = number of turns per cm. on primary.
N' = total number of turns on secondary.
l_1 = length of primary.
d_1 = diameter of primary.
n = number of turns per centimeter on H.
l_2 = length of H.
d_2 = diameter of H.
m = mass of C.
V = volume of C.
d = deflection of galvanometer when C is jerked out of H.
d' = deflection when current is made or broken through primary.
I' = current in amperes through primary.

The advantage of using σ rather than I lies in the fact that σ is independent of changes in density or volume due to changes in temperature. The value of the field H inside the ellipsoid for an external field of H_0 is[1]

$$H = H_0 - LI,$$

where L is the demagnetizing factor of the ellipsoid.

EXPERIMENTAL DETAILS.

Magnet.—The magnetic field was obtained by means of a large electromagnet of the duBois type. The core was approximately 10 cm. in diameter. For this work it was equipped with a pair of conical pole pieces 2.5 cm. in diameter at the smaller end. A hole 2.1 cm. in diameter

[1] Maxwell, Treatise on Electricity and Magnetism, 3d Ed., Vol. II., §437–438, pp. 66–69.

was drilled through these to permit the ellipsoid to be withdrawn. The magnet would carry 25 amperes for several minutes without undue heating. For each air-gap used, the strength of the field at the center was determined by means of a flip coil and ballistic galvanometer calibrated by comparison with a standard helix. The field was also measured with a magnetic balance made by Weber in Zurich and practically identical with the one described by Weiss.[1] The results obtained by the two methods were in close agreement. For convenience, the value of the field for currents from 2 to 25 amperes was determined by steps of two or three amperes. From these data curves were plotted giving H as a function of the current, the scale being such that 1 cm. was equivalent to 100 or 200 lines per square centimeter.

Galvanometer.—The galvanometer used was a Leeds and Northrup type H instrument. It had a resistance of 26.4 ohms, a ballistic sensibility of 45.6 mm. per microcoulomb on open circuit with a scale distance of 50 cm., and a period of 12.7 seconds on open circuit. The scale used had 500 divisions in a length of 25 cm. and was made by photography from a very accurate 50 cm. scale. The sensitiveness was further increased by placing the scale at a distance of approximately three meters. With this arrangement the "throw" could be read accurately to 0.5 of a scale division or even less. As the instrument as used was on closed circuit, it was practically aperiodic, and its sensitiveness was considerably reduced.

Heating Apparatus.—The induction helix was used as the core around which was built up a small electric furnace to give the necessary temperatures. For various reasons two separate pieces of apparatus were built, one for the lower temperatures, the other for the higher temperatures.

Up to 550° C. the apparatus shown in section in Fig. 2 was used. The induction helix was of No. 30 bare copper wire wound on a hard glass tube. The wire was held in place by cæmentium and, where necessary, fibers of asbestos were worked in between the individual turns. There were 89 turns in a length of 4 cm.

The heating coils were of No. 16 german silver wire and were insulated from the induction helix by a glass tube as shown. In order to decrease the temperature gradient at the center of the induction helix, two heating coils were used. The inner one was wound as regularly as possible, while the outer one was wound closely at the ends but with the turns much farther apart at the middle. The two coils were separated from each

[1] Journal de Physique, *36*, pp. 432–435, 1907. See also L'Eclairage Electrique, *24*, pp. 257–266, 1900, and Journal de Physique, *29*, pp. 383–390, 1900.

other by mica. In order to reduce the magnetic effect of the heating currents, the two coils were always connected so that they opposed each other magnetically. By properly adjusting the currents in the two coils, the temperature at the center of the helix could be made constant to within 2° C. over a distance of 10 to 15 mm. The coils were packed in loose asbestos, and the whole apparatus was covered with asbestos board.

Owing to the fact that at the higher temperatures saturation is reached at lower fields, the apparatus used for temperatures above 550° C. was

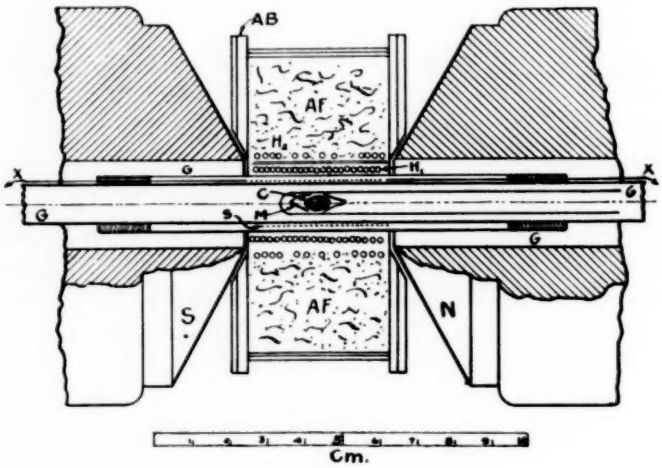

Fig. 2.

S, induction helix; H_1, primary heating coil; H_2, secondary heating coil; *NS*, magnet; *C*, cobalt ellipsoid; *AB*, asbestos board; *AF*, asbestos fiber; *GG*, glass tubes; *M*, mica; *XX*, galvanometer circuit.

somewhat larger though of similar design. The core of the induction helix was a clear quartz tube. The helix was of No. 30 bare platinum wire wound in two layers separated from each other by mica. The individual turns were separated from each other by asbestos yarn. Though the insulating power of this broke down considerably above 1000° C., actual tests showed that this did not introduce any appreciable error.

The heating coils were of No. 13 nickel wire and were separated from the helix by a tube of fused silica. Since nickel loses its magnetic properties at 360° C., no error was introduced by its use. The primary heating coil was wound in two layers. Asbestos yarn was used to separate the individual turns, while the layers were insulated from each other by mica. The secondary heating coil consisted of one layer and was wound as in the other apparatus.

Calcined magnesia contained in a porcelain ring was used as an heat insulator next to the coils. Outside of this a layer of magnesia packing such as is used for high pressure steam pipes was used. The whole apparatus was covered with asbestos board. It is shown in section in Fig. 3. The heating coils on this apparatus burned out several times during the course of the experiments but they were rewound and the apparatus rebuilt in substantially the same way each time. The induction helix was not injured in any way.

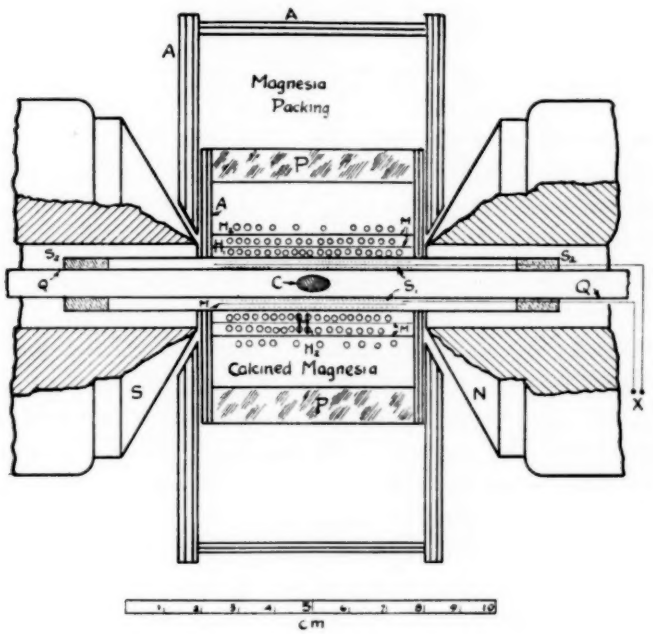

Fig. 3.

S_1, induction helix; S_2, fused silica tube; H_1, primary heating coil; H_2, secondary heating coil; M, mica insulation; A, asbestos board; P, porcelain ring; Q, quartz tube; X, galvanometer circuit.

Temperature Measurements.—Temperatures were measured with a thermocouple. A Wolff potentiometer and Weston standard cell were used to measure its e.m.f., and the resistance in the galvanometer circuit was adjusted so that the instrument read directly to one microvolt. The method of reading and calibration was essentially that described by Clement and Egy.[1] For temperatures between 100° C. and 420° C., a copper-platinum thermocouple was used. As this has an inversion point at about 60° C., it was not used below 100° C. It was calibrated by the boiling point of water, the freezing point of zinc, and by several inter-

[1] Univ. of Ill. Eng. Exp. Station Bulletin No. 36, 1909.

mediate points lying between 120° C. and 250° C. which were determined by comparison with a carefully calibrated mercury thermometer. The temperatures were read from the corresponding e.m.f.'s by a calibration curve plotted to such a scale that 1 mm. corresponded to 1° C.

For temperatures above 420° C., a platinum platinum-rhodium couple was used. This was calibrated at the freezing points of zinc, silver, and copper. From these three points the three constants of the standard parabolic equation were calculated. The couple as used was easily sensitive to 1 microvolt—equivalent to about 0.1° C.—at 1100° C. The temperatures as read from either couple are probably accurate at 1° C.

Preparation and Mounting of the Ellipsoids.—The first samples of cobalt obtained were in the form of small lumps 3 or 4 mm. in diameter. Several attempts were made to fuse these into a button, using first a small assay furnace and later a coke furnace. These attempts proved futile, owing to the very high melting point of cobalt—1489.8° C.

After one or two preliminary trials, a button weighing about 200 grams was prepared from the oxide by the Goldschmidt process. From this two rings were turned and tested by the ring method. The tests on the larger ring—No. 1—gave values of B of only about one tenth the magnitude to be expected. Annealing for several hours at white heat improved this decidedly, though the results were still only about one third of the accepted values. The smaller ring—No. 2—gave similar results without being annealed. Analysis showed that these samples contained about 1 per cent. of aluminum.

One hundred grams of cobalt in rectangular sheets about 6 cm. × 10 cm. × 0.05 cm. were then obtained from Kahlbaum through Eimer and Amend. Tests on a ring—No. 3—made by building up five layers of this showed that its magnetic properties were excellent (see Fig. 4).

To get this material into a form from which ellipsoids could be ground, it was necessary to fuse it into a button or rod. At first this was accomplished by means of a vertical platinum resistance furnace, using a maximum power consumption of approximately 2,200 watts. A No. 0 black lead crucible, lined with a paste of 98 per cent. magnesite and 2 per cent. bone ash, was used. After the lining was thoroughly dry, a charge of about 20 grams of metal was put in and this was covered with a layer of borax glass. After several hours the cobalt fused, giving a very homogeneous button about 2 cm. in diameter and 0.6 cm. thick.

An attempt to repeat the process resulted in burning out the furnace before the cobalt was entirely fused. However one piece was obtained from which it was possible to turn an ellipsoid.

After considerable practice it was found possible to prepare the material

by melting it in a fused silica tube held in an arc. Owing to the impossibility of securing anything like uniform heating over even a short distance, it was only with great difficulty that two or three rods approximately 0.5 cm. in diameter and 1.0 cm. to 1.2 cm. long were obtained by this method.

The ellipsoids were ground from the rods on a Landis Universal Grinder, using an alundum wheel with a properly shaped rim. After grinding, the accuracy of the shape was tested and found to be satisfactory by projecting the enlarged shadow of the ellipsoids with an Edinger Drawing Apparatus.

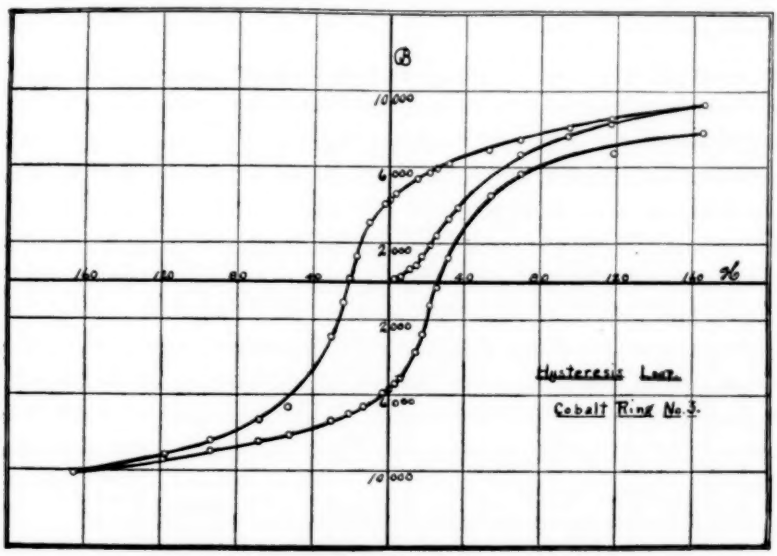

Fig. 4.

In all, five ellipsoids of revolution, approximately 1 cm. long and 0.45 cm. in diameter, were prepared. Complete sets of data, however, were carried out for only two. The ellipsoids were distinguished for convenience as *A*, *B*, *C*, *D*, and *E*. The method of preparing each is given below, and a summary of their dimensions is given in Table I.

A—made from first melting in resistance furnace. Cross-section very accurate.

B—made from the same button as *A*. Not quite as perfect cross-section as *A*.

C—made from rod prepared by melting the metal in fused silica tube held in arc. Cross-section fairly accurate.

D—made from sample melted in silica tube in arc. Cross-section fairly accurate.

E—made from second melting in resistance furnace. Cross-section fairly accurate except for very slight pit near one end.

TABLE I.

	Length.	Mean Diam.	Mass.	Spec. Grav.	Volume by		e	L
					Displac. of Water.	Calculation.		
A	0.9965	0.4475	0.8633	8.25	0.1047	0.1045	0.8934	1.9385
B	0.9330	0.4480	0.8412	8.24	0.1021	0.0981	0.8770	2.0890
C	0.9370	0.4110	0.6804	8.80	0.0773	0.0829	0.8986	1.8888
D	0.9960	0.4430	0.8275	8.74	0.0947	0.1023	0.8956	1.9177
E	0.9920	0.4250	0.8528	8.73	0.0977	0.0938	0.8992	1.8817

In some of the later work, *C* and *E* became more or less oxidized. In each case the oxide was carefully removed with fine emery cloth and the specimen was carefully polished with crocus cloth and weighed. Measurements showed that the shape of the ellipsoids was not altered appreciably by this process.

The reason for the low specific gravity of *A* and *B* is unexplained as yet.

A chemical analysis of the original material showed that it was 100 per cent. pure, with the possibility of a trace of nickel.

For temperatures below 420° C., the ellipsoids were mounted in glass tubes sealed at one end. The thermocouple was inserted through the other end and the junction was separated from the cobalt by a thin layer of mica. As a rule the junction was about one third of the total length

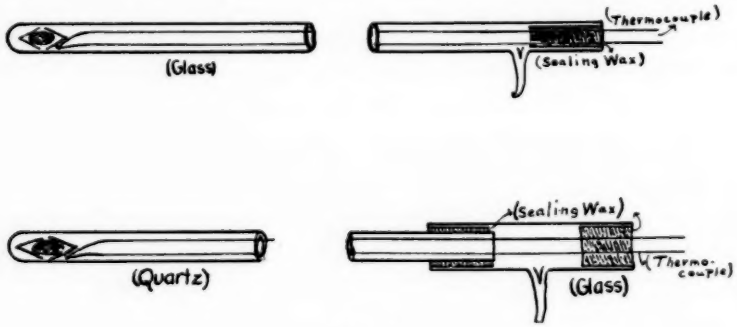

Fig. 5.

of the ellipsoid from the end. For temperatures above 300° C. the end of the tube through which the thermocouple was inserted was sealed with sealing wax, and the whole tube was exhausted and sealed to avoid oxidation of the ellipsoid.

For temperatures above 420° C. a clear quartz tube was used to hold the ellipsoid. A glass tube was joined to the open end of this for con-

venience in exhausting. No particular difficulty was experienced in making the joints air tight with sealing wax, but at the higher temperatures the quartz devitrified upon prolonged heating and the end became "chalky." In this condition it would admit air and in one or two instances as noted above the specimens were oxidized in attempting to carry out a second set of readings. Eventually it was found necessary to re-seal the end of the tube and exhaust the tube anew after each set of readings. Fig. 5 shows the two methods of mounting.

Procedure in Taking Readings.

The general method of taking readings was as follows. The furnace was heated for several hours until thermal equilibrium was established. It was found necessary to draw the heating currents from a large storage battery as the variation of 0.1 ampere caused a very appreciable change in temperature. For the higher temperatures heating currents of 15 to 20 amperes were used. When everything had reached a steady state, the tube containing the ellipsoid and thermocouple was inserted. The position of the tube to bring the ellipsoid into the center of the helix was approximately determined by throwing on the magnetic field for a moment. The tube was then moved by steps of 2 to 5 mm. along the helix, and readings of the temperature at each position were taken after sufficient time had elapsed for the cobalt to take up the temperature of its surroundings. As there is usually comparatively little lag in the readings of a thermocouple, the fact that sometimes as many as twelve or fifteen minutes were required before its readings became constant indicated that the thermocouple was registering the actual temperature of the cobalt. Usually it was possible to adjust the heating currents so that a change of a centimeter in the position of the cobalt produced a change of only 2° or 3° in the readings of the thermocouple. At the lower temperatures it was possible to do much better than this. Under these circumstances, the assumption that the temperature of the ellipsoid was uniform to at least 1° C. seemed justifiable.

The ellipsoid was placed in the position indicated as that at the highest temperature, and the tube was marked so that it was possible to replace it exactly in this position. When the ellipsoid had reached thermal equilibrium, the reading of the thermocouple was taken, the magnetic field was thrown on, and the deflection of the galvanometer when the ellipsoid was jerked out of the helix was noted. The magnetic field was then thrown off and the ellipsoid was replaced in position and allowed to regain its former temperature. As a rule, three readings were taken at each field strength and the mean of the deflections was used in calculat-

ing I and σ. At the lower temperatures these readings usually agreed to half a scale division in two hundred or more. At the higher temperatures they were not so great and the agreement was not quite so good. However the readings as a whole were very consistent even under these circumstances, usually agreeing with each other to within 1 per cent. or at most 2 per cent. up to 900° C. The reading of the thermocouple was taken each time just before the ellipsoid was withdrawn, and—as a rule—these readings were not allowed to differ by more than 15 microvolts, corresponding to 1.5° C., during a set of readings. At the very high temperatures where the cobalt was especially sensitive to changes of temperature, the variation was made even less. The mean of the thermo-couple readings was used in calculating the temperature.

After nearly every set of readings, the galvanometer was calibrated by means of the standard helix. The current, I', for this purpose was read by a Siemens and Halske milliammeter which had been calibrated with a standard ohm coil and potentiometer. For temperatures up to 1000° C., the values of I'/d' remained practically constant and the mean value was used in calculating σ.

The magnetic fields used ranged from 1,600 gausses to 6,900 gausses for the lower temperatures, giving fields of from 800 gausses to 5,000 gausses inside the ellipsoids. As these were insufficient to produce saturation below 350° C., the saturation values were determined by an extrapolation similar to that of Weiss mentioned above. As neither σ and $1/H$ nor σ and $1/H^2$ gave a straight line, both were plotted and the mean of the values was used. The results at these lower temperatures were not used in the theoretical deductions so that extreme accuracy in the extrapolated results is not important. Above 350° C. saturation could be reached with the fields used, and at the higher temperatures fields as low as 3,500 gausses produced saturation. The values of the magnetic field were corrected for the magnetic effect of the heating coils whenever this effect was appreciable.

In the interval between 1050° C. and 1100° C. it was very difficult to obtain consistent readings, as a very slight change in temperature produced a marked change in σ. At these higher temperatures also thermoelectromotive effects in the galvanometer caused some difficulty, rendering the zero of the galvanometer somewhat uncertain at times and often causing it to drift steadily in one direction. These difficulties were remedied in large measure by keeping the junctions of the platinum leads from the helix and the copper connecting wires at 0° C.

Data.

The data obtained for ellipsoids C and E are summarized in the following tables. Tables II. and III. give the values of H and σ as observed at various temperatures, and the values of σ_∞. Table IV. gives a summary of this. Fig. 6 shows the method of determining σ_∞ below 400° C. by extrapolation. The extrapolated values are probably accurate to 1 per cent. Curve A in Fig. 7 shows σ as a function of the temperature. The close agreement between the results for ellipsoids C and E argues for the accuracy of the data.

From the data we can also calculate B and draw magnetization curves for high fields at various temperatures. Several of these curves are shown in Fig. 8.

Theoretical Considerations.

In his article upon the magnetic properties of bodies at high temperatures to which reference was made above, Curie called attention to the

Table II.

Ellipsoid C.

22° C.		120° C.		235° C.		307° C.		414° C.	
H	σ	H	σ	H	σ	H	σ	H	σ
725	102.4	713	103.0	625	108.4	500	115.9	460	119.2
1,955	139.6	2,154	114.2	1,984	149.2	1,980	149.6	2,055	145.8
2,985	149.1	3,031	151.5	3,026	151.8	3,060	149.9	3,135	146.3
3,450	153.2	3,774	153.5	3,816	152.5	3,825	150.4	3,930	146.4
3,955	154.6	4,200	153.3	4,386	152.8	4,425	150.4	4,515	146.4
4,270	155.2								
σ_∞[1] = 161.0		σ_∞[1] = 158.5		σ_∞[1] = 154.0		σ_∞[1] = 151.0		σ_∞ = 146.4	
542° C.		698° C.		874° C.		991° C.		1043° C.	
H	σ	H	σ	H	σ	H	σ	H	σ
445	120.2	140	87.5	215	83.4	370	72.3	770	46.4
2,160	139.9	855	124.1	1,300	97.9	1,680	72.1	2,070	47.5
3,250	139.6	1,620	124.3	2,015	97.9	2,385	73.1	2,780	49.1
4,015	140.2	2,115	125.2	2,510	98.7	2,880	73.3	3,290	48.9
4,610	140.0	2,400	124.9	3,915	97.9	3,335	71.9	3,680	49.5
σ_∞ = 140.2		σ_∞ = 125.2		σ_∞ = 98.7		σ_∞ = 73.3		σ_∞ = 49.5	
1065° C.		1082° C.		1104° C.		1152° C.			
H	σ	H	σ	H	σ	H	σ		
1,165	21.4	3,250	6.0	1,400	1.3	1,370	?		
2,400	26.8			2,400	1.9	2,380	?		
3,060	30.0			3,050	2.6	3,090	?		
3,570	29.7					3,390	?		
4,010	29.4								
σ_∞ = 30.0		σ_∞ = 6.0		σ_∞ = 2.6(?)		σ_∞ = ?			

[1] By extrapolation from curves.

TABLE III.

Ellipsoid E.

22° C.		127° C.		232° C.		300° C.		415° C.		590° C.	
H	σ	H	σ	H	σ	H	σ	H	σ	H	σ
490	66.6	876	94.3	720	103.9	540	114.6	650	108.9	690	106.8
1,285	104.6	2,190	138.6	2,050	147.0	2,175	145.6	2,160	142.2	2,305	132.7
2,575	134.2	3,135	147.1	3,115	148.3	3,140	146.8	3,240	141.6	3,385	133.0
3,260	142.6	3,905	148.9	3,930	149.6	3,970	146.8	3,990	142.6	4,155	133.4
4,065	148.3	4,225	149.5	4,930	149.0	4,505	147.3	4,625	141.2	4,760	132.9
4,445	149.6										
$\sigma_\infty{}^1 = 161.0$		$\sigma_\infty{}^1 = 154.0$		$\sigma_\infty{}^1 = 150.5$		$\sigma_\infty{}^1 = 148.0$		$\sigma = 142.3$		$\sigma_\infty = 133.1$	
687° C.		867° C.		1029° C.		1057° C.		1113° C.		1144° C.	
165	81.2	200	78.7	710	53.0	850	34.7	3,800	3.5	1,420	?
830	121.4	1,210	97.3	1,850	57.8	2,750	38.4			2,440	?
1,515	121.9	1,950	96.3	1,590	56.8	3,185	38.4			3,360	?
2,055	122.0	2,450	96.3	3,160	53.1						
2,450	122.5	2,850	97.5	3,570	53.5						
$\sigma_\infty = 122.5$		$\sigma_\infty = 97.5$		$\sigma_\infty = 57.0$		$\sigma_\infty = 38.4$		$\sigma = 3.5$		$\sigma = ?$	

TABLE IV.

Saturation value of σ as a function of the temperature.

Ellipsoid *C.*		Ellipsoid *E.*		Ellipsoid *C.*		Ellipsoid *E.*	
Temp.	σ_s	Temp.	σ_s	Temp.	σ_s	Temp.	σ_s
22°	161.0	22°	161.0	874°	98.7	867°	97.5
120°	158.5	127°	154.0	991°	73.3	1,029°	57.0
235°	154.0	232°	150.5	1,043°	49.5	1,057°	38.4
307°	151.0	300°	148.0	1,065°	30.0	1,113°	3.5
414°	146.4	415°	142.3	1,082°	6.0	1,144°	?
542°	140.2	590°	133.1	1,104°	2.2		
698°	125.2	687°	122.5	1,152°	?		

similarity between the curves showing I as a function of the temperature for iron and nickel on the one hand, and the curves showing the relation between the density of a vapor and the temperature on the other hand. Langevin[2] a little later worked out on the electron theory a mathematical theory of paramagnetism based upon the assumption that the molecules of a paramagnetic substance obey the gas law. Weiss[3] extended this theory to explain the phenomena of ferromagnetism by the aid of the analogy pointed out by Curie. The sudden increase of density when a vapor liquefies is due to the fact that an enormous internal pressure is

[1] By extrapolation from curves.

[2] Ann. de Chim. et de Phys., Ser. 5, *8*, pp. 70–127, 1905.

[3] Journal de Physique, *36*, pp. 661–690, 1907.

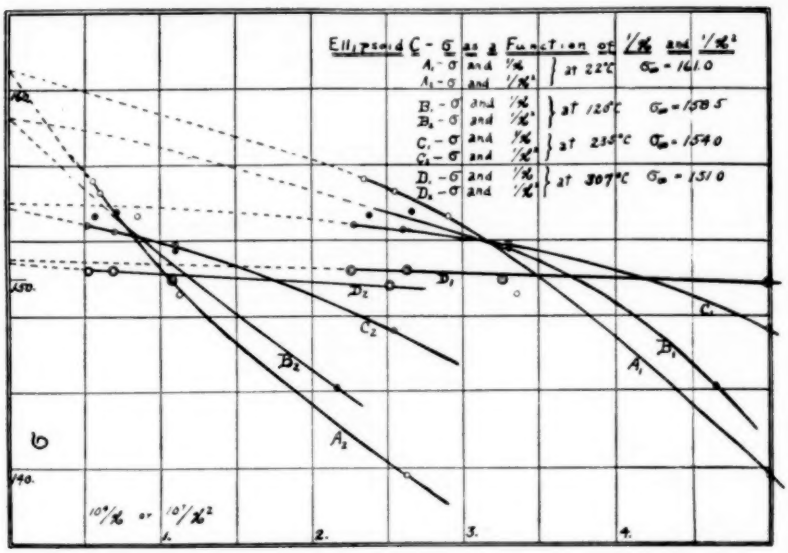
Ellipsoid C - G as a Function of 1/χ and 1/χ²
A1 - σ and 1/χ
A2 - σ and 1/χ²
at 22°C σm = 161.0
B1 - σ and 1/χ
B2 - σ and 1/χ²
C1 - σ and 1/χ
C2 - σ and 1/χ²
at 128°C σm = 158.5
at 235°C σm = 154.0
D1 - σ and 1/χ
D2 - σ and 1/χ²
at 307°C σm = 151.0
150.
140.
10³/χ or 10⁵/χ²
1.
2.
3.
4.
b

Fig. 6.

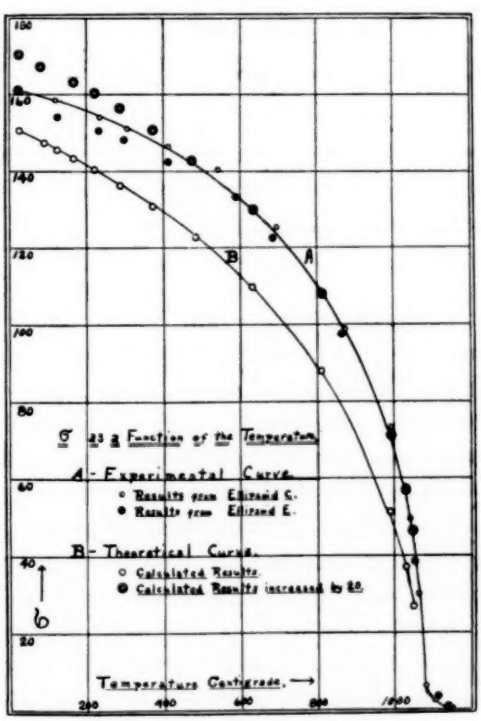
160
140
120
100
80
60
40
20
B
A
σ as a Function of the Temperature.
A - Experimental Curve.
○ Results from Ellipsoid C.
● Results from Ellipsoid E.
B - Theoretical Curve.
○ Calculated Results.
● Calculated Results increased by 20.
b
Temperature Centigrade. →
200
400
600
800
1000

Fig. 7.

suddenly brought into play in addition to the external pressure. Similarly Weiss explained the fact that the ferromagnetic properties suddenly appear when the temperature is lowered below a certain critical temperature by assuming that a strong molecular field is suddenly made operative. This field is due to the action of the molecules upon each other and is called by Weiss the "intrinsic molecular field." Of course the analogy is not perfect for if it were we should expect the pressure-density curves at constant temperature to show the phenomenon of hysteresis. Weiss has calculated the value of this intrinsic field for iron, nickel, and magnetite. Kunz[1] has extended this work by calculating the moments of the elementary magnets.

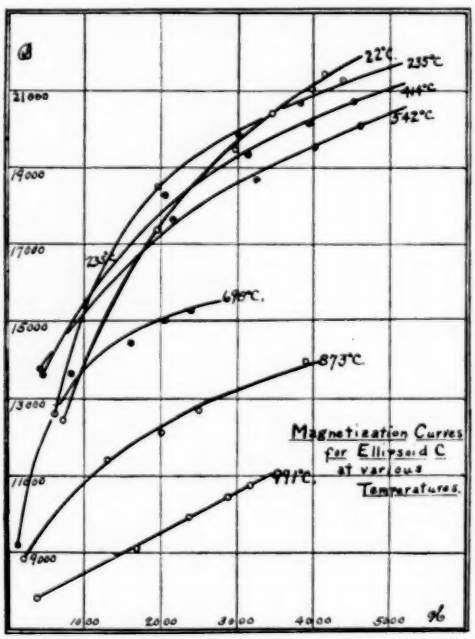

Fig. 8.

Before outlining the theory as developed by these investigators, the terms diamagnetic, paramagnetic, and ferromagnetic as used in this article will be defined.

Diamagnetic substances are those in which the induced polarity opposes that of the inducing field.

Paramagnetic substances are magnetized feebly in the direction of the magnetizing field. The susceptibility is independent of the field strength and is inversely proportional to the absolute temperature according to Curie.

Ferromagnetic substances are very strongly magnetized in the direction of the magnetizing field. The susceptibility is a very complicated function of the field strength and the temperature. The phenomena of hysteresis are characteristic of ferromagnetic substances.

The phenomena of diamagnetism are accounted for by assuming that each atom contains at least one electron revolving in an orbit which lies wholly within the atom. The orbits of the electrons are so arranged that their external moment is zero. Since temperature affects the molecule rather than the atom, the purely diamagnetic properties should be in-

[1] PHYS. REV., *30*, pp. 359–370, 1910.

dependent of the temperature. It is probable that even the paramagnetic and ferromagnetic bodies also contain electronic orbits which give them diamagnetic properties, but the effect is masked by the stronger opposing phenomena.

In the paramagnetic and ferromagnetic bodies, the revolving electrons are so arranged that there is no resulting external moment. Curie[1] showed experimentally for a number of paramagnetic bodies that the paramagnetic susceptibility, $k = I/H$, is inversely proportional to the absolute temperature. This is known as Curie's Law. Langevin, in his article to which reference has already been made, has given a theoretical deduction of this law. Though some very recent experimental results[2] seem to contradict Curie's Law, still on the whole it agrees with the experimental facts in a large number of cases.

The present theory as developed by Langevin, Weiss, and Kunz may be outlined as follows. In a gas at uniform temperature, not subject to the action of gravity, the density is uniform throughout. If gravity is suddenly allowed to act upon the gas, a rearrangement of the molecules occurs; the lower layers of the gas become more dense, and the temperature of the gas rises, due to the fact that a certain amount of potential energy has been converted into kinetic energy—*i. e.*, into heat. The change of pressure with height after equilibrium is established is now given by the familiar exponential law

$$p = p_0 e^{-\rho_0 x / p_0},$$

where p_0 and ρ_0 are the pressure and density respectively at the lowest layer, and x is the height. This law has been generalized by Boltzmann[3] in the form

$$p = p_0 e^{W/RT},$$

where W is the change in the potential energy per unit distance and T and R are respectively the absolute temperature and the universal gas constant.

The arrangement of the molecules in a paramagnetic substance when not under the influence of an external magnetic field is exactly analogous to that of the gas molecules when not under the influence of gravity, and the rearrangement caused by the action of a uniform magnetic field will follow an exactly similar law. The number of molecules, dn, the

[1] Ann. de Chim. et de Phys., Ser. 7, 5, pp. 289–405, 1895; Œuvres, pp. 232–334.

[2] du Bois and Honda, Konink. Akad. Wetensch., Amsterdam, Proc. *12*, pp. 596–602, March, 1910.

[3] Vorlesungen über Gas-Theorie, 1 Teil, p. 136.

directions of whose axes are included in an elementary solid angle, $d\omega$, will therefore be given by

$$dn = Ke^{W/RT}d\omega, \tag{1}$$

where K is a constant. The potential energy of an elementary magnet of moment M whose axis makes an angle Φ with a uniform magnetic field H is

$$W = HM \cos \Phi.$$

But

$$d\omega = 2\pi \cdot \sin \Phi \cdot d\Phi.$$

Substituting this value and integrating from 0 to π we have

$$n = \frac{4\pi K}{a} \sinh a, \tag{2}$$

where

$$a = \frac{HM}{RT}.$$

This result assumes that the resulting intensity of magnetization is in the same direction as H. In general this will not be the case. If Φ is the angle between H and I we have

$$dI = M \cos \Phi \, dn$$

and

$$I = \int_0^\pi M \cos \Phi \, dn.$$

Substituting the value of dn from (1) and integrating, and then substituting the value of K from (2) we have

$$I = nM \left(\frac{\cosh a}{\sinh a} - \frac{1}{a} \right),$$

where n is the number of molecules in unit volume. Since it is the thermal agitation of the molecules which opposes the action of H, if there were no thermal agitation—*i. e.*, if the substance were at absolute zero—the intensity of magnetization would be a maximum and we would have

$$I_m = nM.$$

Hence

$$I = I_m \left(\frac{\cosh a}{\sinh a} - \frac{1}{a} \right), \tag{3}$$

Since

$$a = \frac{MH}{RT},$$

this gives

$$I = I_m \cdot f\left(\frac{H}{T}\right).$$

For paramagnetic substances, a is very small—much less than unity. For values of a^2 less than π^2, $\frac{\cosh a}{\sinh a} - \frac{1}{a}$ can be developed into a convergent series as follows:

$$\frac{\cosh a}{\sinh a} - \frac{1}{a} = \frac{1}{3}a - \frac{2}{90}a^3 + \frac{4}{45 \cdot 42}a^5 \cdots$$

For values of a less than 0.7, the terms of this series involving higher powers of a than the first are negligible, and we have

$$I = \frac{a}{3} I_m,$$

$$= \frac{M^2 nH}{3RT},$$

$$= kH.$$

where k is constant for constant temperature. k is the paramagnetic susceptibility and is seen to be inversely proportional to T, as found by Curie experimentally.

In the case of ferromagnetic substances we have, in addition to the external field, an internal or molecular field, H_m. If this field acted alone, the intensity of magnetization would be proportional to it and we would have

$$H_m = NI,$$

and

$$a = \frac{MH}{RT},$$

$$= \frac{MNI}{RT}.$$

Whence

$$I = \frac{aRT}{MN}, \qquad (4)$$

where N is the factor of proportionality. Equation (4) shows that at any given temperature I is proportional to a.

For any temperature below that at which the spontaneous ferromagnetism disappears, the value of I must satisfy both equations (3) and (4). Plotting equation (3) we have the curve OCA of Fig. 9, while equation (4) gives the straight line OA. Obviously the values of I corresponding to

the origin and to the point A satisfy (3) and (4) simultaneously. The value for the origin is for $I = 0$. Hence the value of I which we wish is that for the point A.

The line OA corresponds to some particular temperature T, and as T varies, OA rotates about the point 0. If Θ denotes the temperature at which the spontaneous ferromagnetism disappears, the tangent to the curve at the origin corresponds to $T = \Theta$.

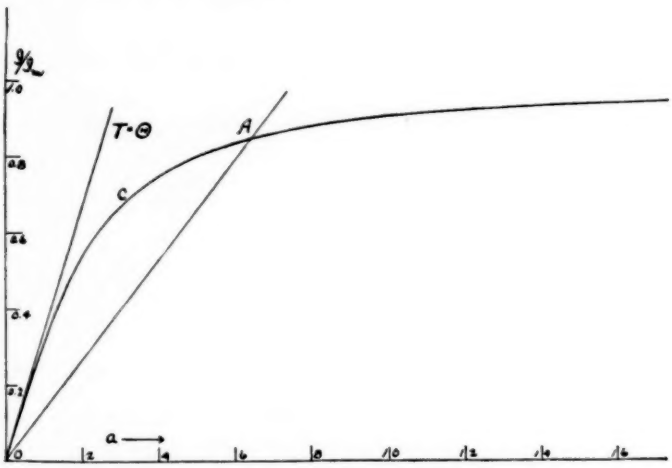

Fig. 9.

From a knowledge of the properties of a body in the neighborhood of Θ it is possible to calculate H_m, the intrinsic molecular field, and M, the moment of the elementary magnet. These calculations have been made for iron, nickel and magnetite. The results are given in Table V., which is taken from Kunz's[1] article.

TABLE V.

Substance.	I at 20° C.	I_m	Θ	N	$NI = H_m$	$M \times 10^{20}$
Fe	1,860	2,120	756° C.	3,850	6,560,000	5.15
Fe_3O_4	430	490	536° C.?	33,200	14,300,000	2.02
Ni	500	570	376° C.	12,700	6,350,000	3.65

In order to make similar deductions for cobalt from the experimental data, the method of calculating these quantities will be indicated. In the neighborhood of the point at which spontaneous ferromagnetism disappears, we have both the external field, H_e, and the internal molecular

[1] PHYS. REV., 30, pp. 359–370, 1910.

field, H_m, acting. That is

$$a = \frac{MH}{RT} = \frac{M(H_e + H_m)}{RT},$$
$$= \frac{M(H_e + NI)}{RT},$$

or

$$T = \frac{M(H_e + NI)}{aR}. \tag{5}$$

While the body is ferromagnetic we have

$$a = \frac{MH}{RT} = \frac{MNI}{RT}. \tag{6}$$

For values of a less than 0.7, the curve for

$$\frac{I}{I_m} = \frac{\cosh a}{\sinh a} - \frac{1}{a}$$

is a straight line, and we may take

$$\frac{I}{I_m} = \frac{a}{3}$$

and

$$I = \frac{a}{3} I_m. \tag{7}$$

This condition will certainly hold for $T = \Theta$. Hence, putting $T = \Theta$ in (6) we have

$$a = \frac{MNI}{R\Theta},$$

$$= \frac{MNI_m a}{3R\Theta}.$$

Hence

$$\Theta = \frac{MNI_m}{3R}. \tag{8}$$

Dividing (5) by (8) we have

$$\frac{T}{\Theta} = \frac{3H_e}{aNI_m} + \frac{3}{a}\frac{I}{I_m},$$
$$= \frac{3H_e}{aNI_m} + 1,$$

or

$$\frac{T - \Theta}{\Theta} = \frac{H_e}{NI},$$

by (7). Hence

$$(T - \Theta)I = \frac{H_e}{N}\Theta. \tag{9}$$

Equation (9) represents an hyperbola. The curves giving I as a function of T for iron show this between 756° C. and 920° C.

To calculate H_m, the value of N is necessary. This may be determined from (9) by taking corresponding values of I and H_e at some temperature above Θ. Solving (9) for N we have

$$N = \frac{H_e}{I}\frac{\Theta}{T - \Theta},$$

$$= \frac{1}{k}\frac{\Theta}{T - \Theta}. \tag{10}$$

N may also be calculated from a knowledge of Curie's constant, C. By Curie's Law we have

$$C = \chi T = \frac{k}{d}T,$$

where χ is the specific susceptibility, and d is the density. But

$$k = \frac{I}{H} = \frac{I}{H_e + NI}.$$

At $T = \Theta$, H_e is negligible in comparison with N. Hence for this temperature

$$k = \frac{1}{N},$$

or

$$C = \frac{1}{N \cdot d}\Theta,$$

or

$$N = \frac{d \cdot C}{\Theta}. \tag{11}$$

Having N we can calculate H_m, taking $I = I_m$, giving

$$H_m = NI_m.$$

From (8) we may obtain M, the moment of the elementary magnet, *viz.*,

$$M = \frac{3R\Theta}{NI_m} = \frac{3R\Theta}{H_m}. \tag{12}$$

Furthermore we may calculate the number of atoms which make up an elementary magnet. Let N' be the number of molecular magnets per

cubic centimeter. Then

$$N'M = I_m$$

or

$$N' = \frac{I_m}{M}. \tag{13}$$

If there are n atoms per elementary magnet and each atom has a mass of m grams, then

$$nN'm = \text{mass per unit volume} = d.$$

But

$$m = Am_H,$$

where A is the atomic weight of the substance and m_H is the mass of the hydrogen atom. Hence we have

$$n = \frac{d}{N'm} = \frac{d}{AN'm_H}. \tag{14}$$

Application of Theory to Experimental Results.

Curve A of Fig. 7, showing σ as a function of the temperature, indicates that the Curie point is in the neighborhood of 1075° C. or 1348° Abs. From this value a theoretical curve giving σ as a function of T can be calculated as follows. The curve OA in Fig. 9 gives us the relation between I/I_m, equal to σ/σ_m, and the parameter a, and Table VI gives the values of σ/σ_m, calculated from equation (3) for various values of a. Hence if we can determine the value of T corresponding to a given value of a, we can at once determine the corresponding value of σ/σ_m either from Table VI or graphically from the curve of Fig. 9. Knowing σ_m we can then calculate the value of σ for the given value of T.

This relation between T and a comes from equation (4) which may be written in the form

$$\frac{I}{I_m} = \frac{\sigma}{\sigma_m} = \frac{R}{MNI_m} aT.$$

From equation (8) we have

$$\Theta = \frac{MNI_m}{3R}.$$

Hence

$$\frac{\sigma}{\sigma_m} = \frac{1}{3\Theta} aT,$$

and

$$T = \frac{3\Theta}{a} \frac{\sigma}{\sigma_m}.$$

This gives us the required equation, and the values of σ/σ_m are given in Table VI.

TABLE VI.

a	$\frac{\cosh a}{\sinh a}$	$\frac{1}{a}$	$\frac{\sigma}{\sigma_m} = \frac{\cosh a}{\sinh a} - \frac{1}{a}$
0.01	100.0000	100.0000	0.0000
0.1	10.0299	10.0000	0.0299
0.2	5.0676	5.0000	0.0676
0.3	3.4328	3.3333	0.0995
0.4	2.6317	2.5000	0.1317
0.5	2.1639	2.0000	0.1639
0.6	1.8619	1.6667	0.1952
0.7	1.6546	1.4286	0.2260
0.8	1.5059	1.2500	0.2559
0.9	1.3961	1.1111	0.2850
1.0	1.3131	1.0000	0.3131
1.2	1.1995	0.8333	0.3662
1.4	1.1295	0.7143	0.4152
1.6	1.0849	0.6250	0.4599
1.8	1.0561	0.5556	0.5005
2.0	1.0373	0.5000	0.5373
3.0	1.0049	0.3333	0.6716
4.0	1.0007	0.2500	0.7507
5.0	1.0000	0.2000	0.8000
6.0	1.0000	0.1667	0.8333
7.0	1.0000	0.1429	0.8571
8.0	1.0000	0.1250	0.8750
9.0	1.0000	0.1111	0.8889
10.0	1.0000	0.1000	0.9000
12.5	1.0000	0.0800	0.9200

As noted above, the work of Weiss and Onnes shows that the value of σ at the temperature of liquid hydrogen is less than 163.6. Assuming this value for σ_m, the values of σ and T corresponding to various values of the parameter a can be calculated. Thus, for $a = 0.5$

$$\frac{\sigma}{\sigma_m} = 0.1639,$$

from Table VI. Hence

$$\sigma = 0.1639 \times 163.6 = 26.8$$

and

$$T = \frac{3 \times (1{,}075 + 273)}{0.5} \times 0.1639 = 1326^\circ \text{ Abs.} = 1053^\circ \text{ C.}$$

Carrying out similar calculations for other values of a the results given in Table VII. are obtained. In this table, t is the centigrade temperature corresponding to the absolute temperature T.

TABLE VII.

a	σ/σ_m	T	σ	t
0.5	0.1639	1326°	26.8	1053°
0.7	0.2260	1306°	37.0	1033°
1.0	0.3131	1266°	51.2	993°
2.0	0.5373	1086°	87.9	813°
3.0	0.6716	905°	109.9	632°
4.0	0.7507	759°	122.8	486°
5.0	0.8000	647°	130.9	374°
6.0	0.8333	562°	136.3	289°
7.0	0.8571	495°	140.2	222°
8.0	0.8750	442°	143.2	169°
9.0	0.8889	399°	145.4	126°
10.0	0.9000	364°	147.2	91°
12.5	0.9200	298°	150.5	25°

The values of σ and t from Table VII. are plotted in curve B of Fig. 7. This curve is of the same general shape as the experimental curve, A, but it lies entirely below A. The difference between the two curves is about 10 at 0° C. and increases gradually to 20 at 600° C. From this point on up to 1050° C. the difference between the two curves at any temperature is practically constant, lying between 20 and 21. Hence if the theoretical curve is shifted up 20 divisions it will coincide with the experimental curve in the interval 500° C. to 1050° C. This is shown by the double circles in Fig. 7.

In the interval above 1070° C. the experimental curve has the general form of the hyperbola. This agrees with the requirements of equation (9).

From the data at 1104° C. we can calculate the molecular field and the moment of the elementary magnet. For this temperature we have

$$T = 1104° + 273° = 1377° \text{ Abs.}$$
$$I_m = 163.6 \times 8.77 = 1{,}435.$$

H_e	I	I/H_e
1,400	11.1	0.00793
2,400	16.6	0.00692
3,050	23.3	0.00764

Mean value of $I/H_e = k = 0.00753$.

Substituting these values in equation (10) we have

$$N = \frac{1}{0.00753} \times \frac{1{,}348}{1{,}377 - 1{,}348} = 6{,}180.$$

Hence

$$H_m = NI_m = 6{,}180 \times 1{,}435 = 8{,}870{,}000.$$

From equation (12) we have

$$M = \frac{3R\Theta}{NI_m}.$$

The value of R to be used is that corresponding to one molecule, *viz.*, $R = 1.36 \times 10^{-16}$. Hence

$$M = \frac{3 \times 1.36 \times 10^{-16} \times 1{,}348}{6{,}180 \times 1{,}435} = 6.21 \times 10^{-20}.$$

The number of elementary magnets per cubic centimeter from equation (13) is

$$N' = \frac{I_m}{M} = \frac{1{,}435}{6.36 \times 10^{-20}} = 2.31 \times 10^{22}.$$

The number of atoms making up an elementary magnet is given by equation (14), *viz.*,

$$n = \frac{d}{N'm} = \frac{d}{N'Am_H}.$$

The values to be substituted are:

$$d = 8.77, \qquad N' = 2.31 \times 10^{22},$$
$$A = 59.00, \qquad m_H = 1.61 \times 10^{-24},$$

giving

$$n = \frac{8.77}{59.00 \times 2.31 \times 10^{22} \times 1.61 \times 10^{-24}} = 4.01.$$

Hence four atoms of cobalt make up the elementary magnet. The value 4.01 is far more nearly an exact integer than the accuracy of the data would lead us to expect, and this is strong evidence of the accuracy of the value of Θ.

It is interesting to compare these results with those given in Table V. The results are summarized in Table VIII.

TABLE VIII.

	I at 20° C.	I_m	Θ	N	$NI_m = H_m$	$M \times 10^{20}$	n	N'
Fe	1,860	2,120	756° C.	3,850	6,560,000	5.15	2	4.12×10^{22}
Ni	500	570	376° C.	12,700	6,350,000	3.65	6	1.56×10^{22}
Co	1,421	1,435	1,075° C.	6,180	8,870,000	6.21	4	2.31×10^{22}

As was to be expected, the values of I and I_m for cobalt lie between the corresponding values for iron and nickel. The same is true of N and N'.

Θ however is much higher, while the intrinsic molecular field is one third larger than that of iron or nickel, and the moment of the elementary magnet is one fifth larger than that of iron and two thirds larger than that of nickel.

It is very interesting to note that the elementary magnet of cobalt consists of four atoms while the elementary magnet of iron, as indicated by the work of Kunz, consists of two atoms and that of nickel of six atoms.

Using the laws of electrolysis, another important physical constant can be calculated, namely the elementary charge, e. This is done as follows. The number of atoms per cubic centimeter of cobalt is

$$\bar{N}' = nN'.$$

Hence the number of atoms per gram is

$$\bar{N} = \bar{N}'/d = nN'/d$$

and the number of atoms per gram atom is

$$A\bar{N} = nN'A/d.$$

Hence the quantity of electricity required to deposit one gram atom is

$$Q = \frac{nN'A}{d} \cdot v \cdot e,$$

where v is the valency. But from the laws of electrolysis

$$\begin{aligned} Q &= v \cdot 96{,}540 \text{ coulombs} \\ &= v \cdot 9.65 \times 10^3 \text{ c.g.s. electromagnetic units.} \end{aligned}$$

Hence

$$\frac{nN'A}{d} \cdot v \cdot e = v \cdot 9.65 \times 10^3$$

or

$$e = \frac{9.65 \times 10^3 \times d}{nN'A}.$$

Substituting the values obtained above this gives

$$\begin{aligned} e &= \frac{9.65 \times 10^3 \times 8.77}{4 \times 2.31 \times 10^{22} \times 59} \\ &= 1.55 \times 10^{-20} \text{ c.g.s. electromagnetic units,} \\ &= 4.65 \times 10^{-10} \text{ c.g.s. electrostatic units.} \end{aligned}$$

Until the recent work of Millikan[1] the accepted value for e was $4.65 \times$

[1] PHYS. REV., *32*, pp. 349–397, 1911.

10^{-10} c.g.s. electrostatic units. This exact agreement is certainly far better than would reasonably be expected, and is further evidence of the reliability of the results at high temperatures.

The recent work of Weiss mentioned above gives values for χ for the interval from 1156° C. to 1302° C. Calculations of N, M, H_m, and n based upon his results are in fair agreement with the results deduced above.

SUMMARY.

The chief results of this investigation are the following:

1. The saturation value of the intensity of magnetization of cobalt has been determined at intervals of one hundred to one hundred and fifty degrees throughout the interval from 22° C. to 1150° C.

2. The "Curie Point," or point of magnetic transformation from the ferromagnetic to the paramagnetic state, has been established at 1075° C.

3. The curve giving σ as a function of the temperature has been shown to be of the same general character as that demanded by theory, though differing from the theoretical curve by a constant amount throughout most of its length

4. The values of the intrinsic molecular field, H_m, the moment of the elementary magnet, M, the number of atoms in an elementary magnet, n, and the elementary charge, e, have been calculated and found to have the following values:

$$H_m = 8{,}870{,}000, \qquad n = 4,$$
$$M = 6.21 \times 10^{-20}, \qquad e = 4.65 \times 10^{-10} \text{ E.S.}$$

The author takes pleasure in acknowledging his indebtedness to Professor A. P. Carman for the facilities for this investigation, and to Professor Jakob Kunz both for his general supervision of the work and for many valuable suggestions.

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UNIVERSITY OF ILLINOIS,
May 8, 1911.

THE TRANSVERSE THERMOMAGNETIC EFFECT IN NICKEL AND COBALT.

By Alpheus W. Smith.

IN an earlier paper the author[1] has studied the Hall effect in iron, nickel and cobalt at a number of temperatures between − 190° and 1100° C. For a given magnetic field the Hall effect in these metals was found to increase more and more rapidly, until the critical temperature of the metal in question was reached, where for a small additional increase in temperature the effect sinks suddenly to a small fraction of its value at that temperature and then continues to decrease with further rise of temperature. In each of these metals it is known that there is a molecular change at the critical temperature. The nickel changes from α-nickel to β-nickel; the iron from α-iron to β-iron and then to γ-iron; and the cobalt from α-cobalt to β-cobalt. These molecular transformations manifest themselves also in a change of the electrical resistance,[2] in a change of the thermoelectric heights[3] and in a change in the magnitude of the Peltier effect.[4] These latter changes are, however, not large in comparison with the change in the Hall effect or with the change in the permeability. This behavior of the Hall effect at the critical temperature allies it more closely to the magnetic properties of the metal than to either the resistance or the thermoelectric heights. It seemed of interest to examine some of the other effects which are allied to the Hall effect, in order to see in what way they are influenced by changes of temperature and by the molecular transformations which are known to take place when the metals pass from the magnetic to the non-magnetic state.

For a clear statement of the various phenomena which arise when a metal plate which is carrying either a current of heat or a current of electricity is brought into a magnetic field so that the lines of force are normal to the plane of the plate, reference is made to the paper by H. Zahn[5] and to the paper by Hall and Campbell[6] on these phenomena. For our present purposes it is only necessary to recall that when a metal

[1] Phys. Rev., 30, p. 1, 1910.
[2] Harrison, Phil. Mag. (6), 3, p. 183.
[3] Ibid., p. 192.
[4] Cermak, Ann. der Phys., 24, p. 351, 1907.
[5] Ann. d. Phys., 14, p. 886, 1904.
[6] Proc. Amer. Soc. of Arts and Sci., 46, p. 625, 1911.

plate which is carrying a longitudinal electrical current is brought into a magnetic field so that the lines of force are perpendicular to the plane of the plate, there is set up in the plate a transverse electromotive force whose magnitude is given by the equation,

$$E = R\frac{Hi}{d},$$

where E is the electromotive force in absolute units; H, the magnetic field in absolute units; i, the current in absolute units; d, the thickness of the plate in centimeters.

When a similar plate through which there is a longitudinal flow of heat is brought into a magnetic field in the way indicated above there is set up by the magnetic field a transverse electromotive force given by the equation,

$$E = Q\beta H\frac{\partial T}{\partial x},$$

where E is the electromotive force in absolute units; β, the width of the plate in centimeters; H, the magnetic field in absolute units; $\partial T/\partial x$, the temperature gradient in the plate in degrees Centigrade per centimeter; Q, a constant which is a function of the temperature of the plate and sometimes of the magnetic field. This phenomenon is known as the transverse thermomagnetic effect or as the Nernst effect. Its variation with the temperature of the plate and its relation to the Hall effect and to the magnetic properties form the subject of the present paper.

APPARATUS AND METHOD.

For the study of the transverse thermomagnetic effect between room temperature and 100° C., the apparatus for securing the desired temperature gradient in the plates, was the same as that used by the author[1] in the study of this effect in alloys. It consisted essentially of two copper tubes to each of which was soldered a narrow strip of copper about 0.5 cm. in thickness. To these copper strips were soldered the ends of the plates to be investigated. Through one of the tubes flowed steam at atmospheric pressure; through the other tube, water at room temperature. The plates which were about 4 cm. long, 1.5 cm. wide and 0.1 cm. thick, were cut from a larger sheet of the metal so that narrow arms projecting from the middle of each of the longer edges, extended some distance out of the magnetic field. To the ends of these arms which were filed down until they were about 0.1 cm. in diameter were soldered

[1] PHYS. REV., 32, p. 178, 1911.

the copper lead wires which lead to the galvanometer on which the effect was to be observed. Where the original sheet was not large enough to allow arms of sufficient length to extend out of the magnetic field, the arms were built up out of shorter pieces of the metal by silver-soldering these pieces together. By means of these arms the error due to the transverse galvanomagnetic effect discovered by Leduc[1] is eliminated, for the junction of the lead wire and the plate can not form a thermal couple since both are of the same material. To determine the temperature gradient in the plate a copper-nickel thermal couple was soldered to either end of the plate on a line midway between its upper and lower edges.

To secure the desired temperature gradients in the plate at temperatures above 100° C. an electric heating device was constructed. It consisted essentially of two copper rods *A* and *B* (Fig. 1*a*). These rods

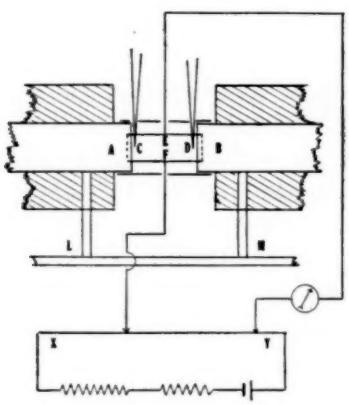

Fig. 1a.

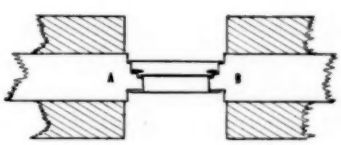

Fig. 1b.

were about 3.5 cm. in diameter and about 13 cm. in length. They were connected by the brass bar *LM* in such a way that they were electrically insulated from each other. Around each of these rods was wrapped two layers of nichrome wire, insulated from each other and from the rods by means of asbestos and strips of mica. The rods and their windings were then covered with a large number of layers of asbestos paper to afford protection against the loss of heat. The coils of nichrome wire were then connected independently to a suitable source of alternating current. By sending suitable currents through these coils any desired temperature gradient could be obtained and the temperature of the plate could be increased or decreased at will. In order to fasten the ends of

[1] Compt. Rend. 104. p. 1785 (1887).

the plates to the ends of the rods, the rods were cut away as indicated in Fig. 1*b* which is a cross section of the rods and plate perpendicular to the plane of the plate. The plate was held in the recess provided for it by means of heavy copper clamps which fastened it firmly to the copper rod. To prevent the lateral flow of heat from the plate and to insure as far as possible a uniform temperature gradient in the plate, it was enclosed in a thin box of non-conducting material. The front and back of the box (Fig. 1*b*) were made of thick sheets of mica which were fastened by means of screws to the ends of the copper rods. The top and bottom of the box were made of heavy asbestos board, also fastened by screws to the ends of the copper rods. This box was about 1.8 cm. thick, 4 cm. high, and about 5.5 cm. long. It was filled with powdered magnesium oxide and when the plate was in position there was between the plate and the walls of the box an insulating layer of this magnesium oxide about 0.8 cm. in thickness.

At *C* and *D* (Fig. 1*a*) was clamped a thermal couple to determine the temperature gradient in the plate. For the lower temperatures copper-nickel thermal couples were used; for higher temperatures, platinum-platinum-iridium couples. From *E* and *F* projected the arms which were cut out of the larger sheet of metal in the manner already described. To these arms were soldered the lead wires which after protection against thermal electromotive forces lead through the galvanometer to the potentiometer *XY* on which the difference of potential between *E* and *F* was measured in the usual way. There was also in the circuit with the galvanometer an auxiliary potentiometer for compensating the thermal electromotive forces that happened to be in the circuit.

The cobalt and the nickel for one of the nickel plates was obtained from Kahlbaum. The nickel for the other nickel plate was furnished by Eimer and Amend and referred to by them as chemically pure.

The plate was placed between the poles of the magnet in the usual manner and rigidly supported. The currents in the heating coils were then regulated until the desired temperature gradient was secured. When the thermal couples showed that temperature equilibrium had been established, the thermal electromotive forces which happened to be in the galvanometer circuit were as nearly as possible compensated and the difference of potential produced between the edges of the plate by the establishment of the magnetic field was then measured. The direction of the magnetic field having been reversed, the corresponding difference of potential was again measured. The mean of these two observations was taken as the electromotive force called forth by the magnetic field. Sometimes the differences of potential obtained for

opposite directions of the magnetic field were not equal, because there was some change in the thermal electromotive forces in the reversal of the magnetic field. It was found, however, that the mean of the observations just described eliminated this dissymmetry. These observations were repeated a number of times for each magnetic field and the mean of these observations has been used in the subsequent figures and tables. The magnetic fields were measured ballistically by comparison with a standard solenoid. For the greater part of the work the temperature gradient in the plate was about 25° C. per centimeter, but in a few cases it had to be somewhat greater or less than 25° C. per centimeter. The mean of the temperatures of the ends of the plate was taken as the temperature of the middle of the plate where the difference of potential was observed.

Results.

The results of these observations on the nickel plate from Eimer and Amend have been plotted in Fig. 2 and those on the plate of Kahlbaum nickel in Fig. 3. The abscissæ in these figures are the magnetic fields in absolute units and ordinates are the corresponding differences of potential reduced to the case of a plate which is 1 cm. wide and has a temperature gradient of 1° C. per cm. in it. From an examination of these figures it is seen that at the lower temperatures the electromotive force is at first proportional to the magnetic field, until the field reaches a value of about 5,000 absolute units. Above such fields a large increase in the magnetic field is accompanied by only small increases in the corresponding difference of potential. With this increase of the magnetic field the Nernst electromotive force seems to approach a limiting value just as the intensity of magnetization approaches a limiting value with an increase of the magnetizing force. As the temperature is increased the fields at which proportionality between the magnetic field and the Nernst electromotive force ceases, become smaller, so that the bends in the curves in Figs. 2 and 3 shift toward the left. It will be noticed from these curves that the fields for this saturated condition are somewhat larger for the plate of Eimer and Amend nickel than for the plate of Kahlbaum nickel. For the same temperature and equal magnetic fields the Nernst electromotive force is in general greater in the nickel plate from Eimer and Amend than in the nickel plate from Kahlbaum. When a temperature of about 350° C. has been reached, the electromotive force for low fields is still increasing with rise of temperature but the electromotive force for high fields where the saturated condition is being reached is less than the corresponding electromotive force for a temperature of about 300° C. At about 370° C. for the plate of nickel from Eimer and

Amend and at about 380° C. for the plate of Kahlbaum nickel the character of the curve relating the Nernst electromotive force and the magnetic field has completely changed. There is still evidence of an approach to the saturated condition but it is not possible to reach that condition with the fields available in these experiments. Above 400° C. the nickel has lost its magnetic properties and the Nernst electromotive force seems to be proportional to the magnetic fields over the range of fields used in these experiments. The magnitude of the effect decreases rapidly for small increases of temperature above the critical temperature, so that at about 400° C. for a magnetic field of about 2,500 absolute units the Nernst electromotive force is only about one twentieth of the corresponding electromotiev force at a temperatur slightly less than the crite ical temperature.

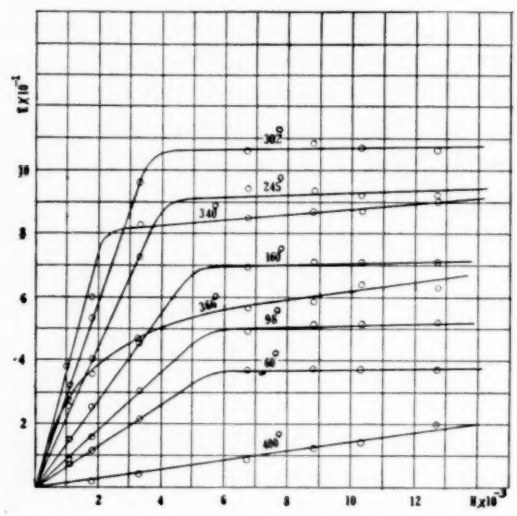

Fig. 2.
Nickel from Eimer and Amend.

The curves given in Figs. 2 and 3 are very similar in character to the corresponding curves relating the Hall electromotive force and the magnetic field. The reason for the shift in the bends in these curves toward lower fields is the same as the reason assigned for the corresponding shift in the bends in the curves for the Hall effect. Both the Hall electromotive force and the Nernst electromotive force seem to be proportional to the intensity of magnetization in the plate rather than to the

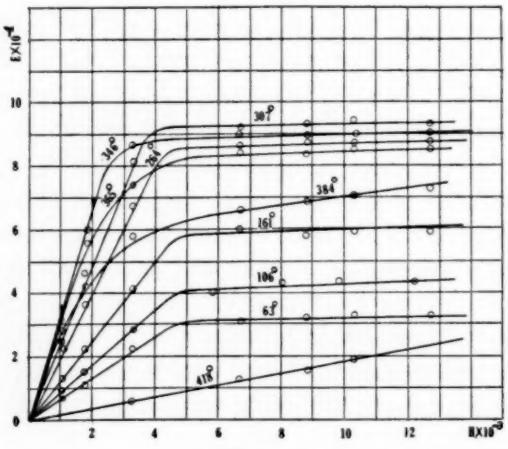

Fig. 3.
Kahlbaum Nickel.

magnetic field, so that when the intensity of magnetization has reached its maximum value the Hall electromotive force and the Nernst electromotive force will reach a maximum value. In nickel the maximum value of the intensity of magnetization decreases continuously with the rise of temperature, at first slowly and then more more rapidly, as the critical temperature is approached. Hence the higher the temperature the lower the field in the air-gap necessary to produce saturation in the plate.

In Fig. 4 the value of Q in the equation $E = Q\beta H \partial T/\partial x$ has been plotted against the absolute temperature of the plate. The values are

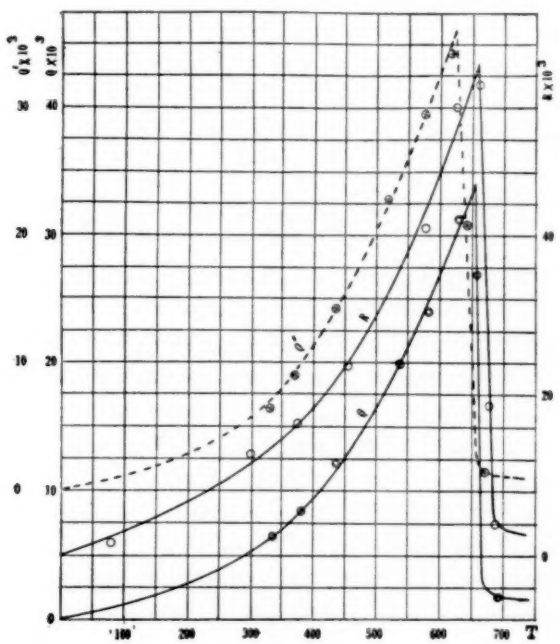

Fig. 4.

Nickel.

plotted for the region where the preceding curves showed that there was a proportionality between the Nernst electromotive force and the magnetic field. The lower curve is for the plate of Kahlbaum nickel; the upper curve for the plate of nickel from Eimer and Amend; the middle curve is taken from the previous paper and shows the relation between the Hall constant R and the absolute temperature. The ordinates on the right refer to the Hall effect; those on the left to the Nernst effect. Q means the constant for the Kahlbaum nickel plate and Q' the constant for the plate of Eimer and Amend nickel. The curves have been displaced vertically in order to avoid superposition. It is seen that the

character of the curve is the same whether it is for the Hall effect or for the Nernst effect. The sudden decrease in the Hall effect and the corresponding decrease in the Nernst effect occur at nearly the same temperature. The curve for Q as well as that for Q' has been extended back to the absolute zero.

Table I. contains the values of Q, Q' and R read off of the curves in Fig. 4 at intervals of fifty degrees between 300° and 650° absolute. In the last column of this table the ratio of Q to R has been tabulated, and in Fig. 7 this ratio is plotted against the absolute temperature. From this ratio it is seen that Q increases more rapidly than R with increase of temperature. The comparison between the values of Q' and R is less certain because the plate in which Q' was determined and that in which R was determined certainly differed somewhat in purity. The results on the nickel plate from Eimer and Amend, however, confirm the results on the Kahlbaum nickel plate. At 32° C. the value of the Nernst effect is nearly the same in the two plates. With rising temperature it increases somewhat more rapidly in the Eimer and Amend plate than in the Kahlbaum plate, but at their respective critical temperatures the magnitude of the effect in both plates is about the same. The critical temperature in the former is reached earlier than in the latter. As the critical temperature is approached the ratio of Q to R approaches a constant value. Nernst[1] found Q to have a value of 8.01×10^{-3} at 56° C. when the magnetic field was about 830. At about the same temperature Zahn[2] gives for one plate of nickel $Q = 1.3 \times 10^{-3}$ when the magnetic field is 10,620; for another plate of nickel he gives for $Q = 3.55 \times 10^{-3}$ when the magnetic field is 6,290. The value given in this paper is larger than the value given by Zahn and less than that given by Nernst. This lack of agreement between the values obtained by different observers may be attributed to impurities in the nickel.

TABLE I.

Nickel.

Abs. Temp.	$R \times 10^3$	$Q \times 10^3$	$Q' \times 10^3$	$Q/R \times 10$
300°	11.2	5.25	5.25	4.69
350	14.8	7.25	7.7	4.90
400	18.8	9.75	11.3	5.19
450	24.0	13.0	16.0	5.42
500	30.2	16.7	21.2	5.53
550	37.6	21.3	26.2	5.67
600	46.8	27.0	32.5	5.77
650	59.0	34.0	—	5.76

[1] W. A., 31, p. 760, 1887.

[2] Ibid., p. 921.

Fig. 5 shows the relation between the Nernst electromotive force in cobalt and the magnetic field. The electromotive force is approximately proportional to the magnetic field over the range of fields used in these experiments. At 56° C. there is a suggestion that the saturated condition is being reached but at higher temperatures it is not possible to reach saturation with the magnetic fields here available. In the work on the Hall effect it was seen that between − 190° C. anda bout 300° C. the fields necessary to obtain saturation increased with rising temperature and for higher temperatures there is a corresponding decrease with rising temperature. The field for which saturation begins to appear at 56° C. in the Nernst effect seems to be nearly equal to the field at which saturation begins to appear in the Hall effect at the same temperature. The shift toward higher fields agrees with the corresponding shift in the Hall effect. The explanation of this shift is the same as that given for the analogous shift in nickel.

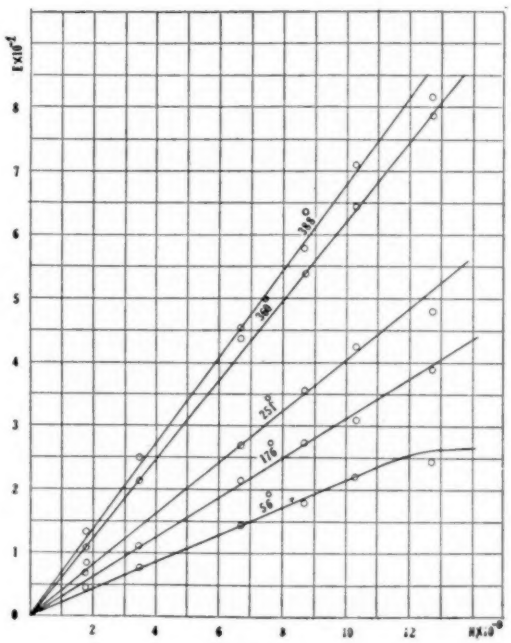

Fig. 5.

Cobalt.

The curves in Fig. 6 show the relation between Q and the temperature and the relation between R and the temperature in cobalt. The abscissæ are temperatures on the absolute scale; the ordinates on the right are for R and those on the left are for Q. The character of the two curves is essentially the same but R increases a little more rapidly than Q, so that the ratio of Q/R decreases with rising temperature. This decrease becomes less rapid at higher temperatures and apparently the ratio approaches a constant value. The values of Q and of R have been read off of these curves at intervals of fifty degrees and the values tabulated in Table II. The last column of that table contains the ratio Q/R. In Fig. 7 this ratio has been plotted against the absolute temperature. Zahn gives for the value of Q in cobalt 1.8×10^{-3}; Nernst found for it

the value 2.24×10^{-3}. The value 1.80×10^{-3} for the plate studied in this paper agrees well with the value given by Zahn.

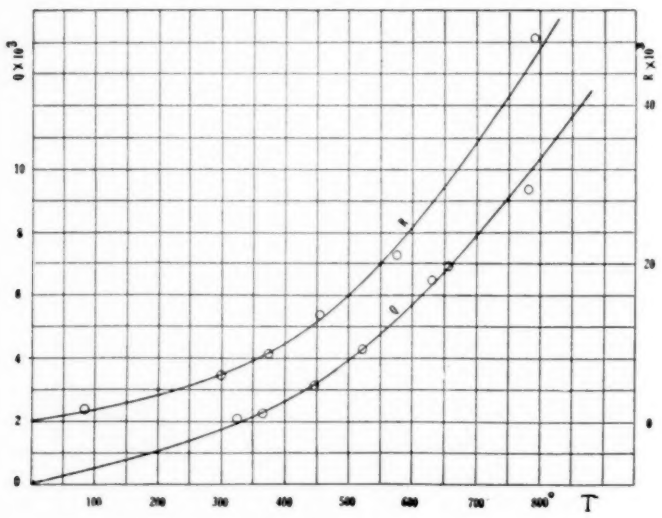

Fig. 6.

Cobalt.

In Fig. 7 besides the curves showing the relation in nickel and cobalt between Q/R and the temperature a similar curve has been plotted for

TABLE II.

Cobalt.

Abs. Temp.	$R \times 10^3$	$Q \times 10^3$	$Q/R \times 10$
300°	5.88	1.80	3.00
350	7.60	2.15	2.83
400	10.0	2.70	2.70
450	12.6	3.30	2.62
500	16.0	4.00	2.50
550	20.0	4.85	2.42
600	24.6	5.70	2.32
650	29.6	6.75	2.28
700	35.0	7.80	2.23
750	40.8	8.90	2.18
800	46.8	10.00	2.16

soft iron from the data of Hall and Campbell.[1] In nickel the least magnetic of these substances Q increases more rapidly than R; in cobalt which is more magnetic than nickel but less mangetic than iron Q in-

[1] Ibid., p. 644.

creases somewhat less rapidly than R; and in iron Q increases much less rapidly than R. It seems that the more magnetic the substance the

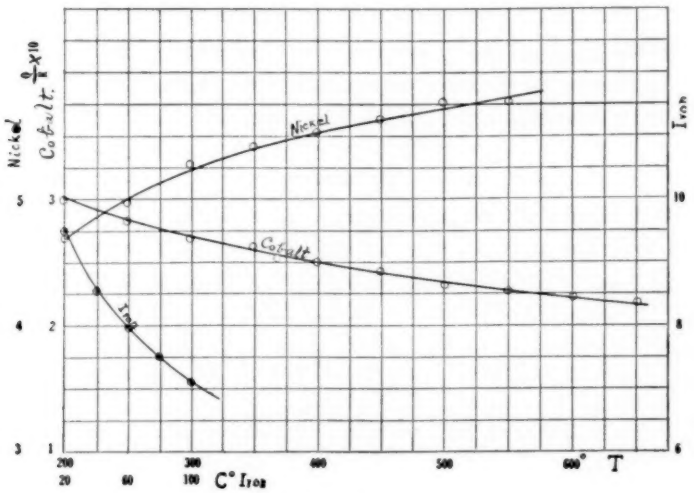

Fig. 7.

more rapid will be the decrease of Q/R with rising temperature and that for a metal no more magnetic than nickel this ratio will increase.

The behavior of the Hall effect and the Nernst effect where the molecular transformation from α-nickel to β-nickel takes place is of interest in connection with the relation between these effects and the resistance and the thermoelectric heights of the metals. Baedeker[1] has called attention to the fact that an increase of resistance is accompanied by an increase in the Hall effect. The author's[2] observations on the Hall effect in alloys points to the same conclusion, but they also make evident that there is not a proportionality between the Hall effect and the resistance in alloys. The data here given together with the data by Harrison[3] on the resistance of nickel shows that the resistance depends on the temperature in a different way from the way in which the Hall effect and the Nernst effect depend upon it. At the critical temperature there is a small decrease in the rate at which the resistance increases with the temperature but there is a marked decrease in the Hall effect and in the Nernst effect. The factors which determine the changes in the former can only determine to a small degree the changes in the latter. A relation between the thermoelectric heights and the Hall effect has been previously pointed out. The

[1] Electr. Erscheinungen in Metallischen Leitern, p. 104.

[2] PHYS. REV., 32, p. 178, 1911.

[3] Phil. Mag. (6), 3, p. 177.

metals which have the largest thermoelectric height with respect to lead have in general the larger Hall effects. The observations of Harrison on the thermoelectric heights of nickel and those of Cernak[1] on the Peltier effect in nickel show in each of these phenomena only small changes at the critical temperature. Neither the Hall effect nor the Nernst effect can be therefore regarded as determined completely by the factors which determine the thermoelectric heights and the Peltier effect.

SUMMARY.

The chief results of this paper are:

1. The relation between the Nernst electromotive force and the magnetic field has been examined in nickel at a number of temperatures between 56° and 410° C. For a given magnetic field it has been found to increase with rising temperature until the critical temperature has been reached. The rate of increase becomes greater the nearer the critical temperature is approached. In passing the critical temperature the Nernst effect sinks to a small fraction of its value at that temperature and then probably decreases with further rise of temperature.

2. For any particular temperature below the critical temperature the Nernst electromotive force is at first proportional to the magnetic field but when the intensity of magnetization approaches its maximum there is a rapid deviation from this proportionality and the electromotive force approaches a limiting value at higher magnetic fields. Since the maximum intensity of magnetization decreases with rising temperature, the fields necessary to produce saturation become less as the temperature is increased.

3. At temperatures above the critical temperature the Nernst electromotive force is proportional to the magnetic field.

4. The study of the Nernst effect in cobalt between 56° and 550° has showed that the Nernst electromotive force is proportional to the magnetic field over that interval of temperature and over the range of magnetic fields in these experiments.

5. In nickel the Nernst effect increases more rapidly than the Hall effect with rising temperature and in cobalt it increases less rapidly than the Hall effect. In this respect cobalt behaves like iron.

[1] Ann. der Phys., 24, p. 351, 1907.

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THE DISTILLATION OF AMALGAMS AND THE PURIFICATION OF MERCURY.

By G. A. Hulett.

Distillation of Amalgams.

In a previous article,[1] it was shown that measurable quantities of some of the common metals distil over with the mercury vapor when they are present with the mercury in the still. It seems that in the distillation of amalgams, just as in the case of other liquid mixtures, that a complete separation is impossible. It was found, however, that when a little air was allowed to pass over with the mercury vapor during the distillation that most metallic vapors were odixized while mercury vapor was not affected. On distilling zinc amalgams with a little air bubbling up through the mercury and passing over with the vapors, no zinc was detected in the distillate although we were able to detect one part of zinc in 10^{10} parts of mercury.[2] Zinc amalgams were also distilled in an ordinary Weinhold still where the air was all displaced by mercury vapor and the distillation was carried on in a space which was free from all gases except mercury vapor. Under these conditions it was always possible to detect zinc in the distillate, even when there was only a trace of zinc in the mercury in the still.

The above experiments suggested that all readily oxidizable metals such as zinc, cadmium, bismuth, tin, copper, lead, etc., might be effectively removed by one distillation. The simplest method of accomplishing this result was to use an ordinary distilling flask with suction and so arranged that a little air bubbled through the mercury in the still and passed over with the vapors. This arrangement, just as for other liquids, prevented the troublesome bumping and spurting of the mercury.[3] The distillation was carried out in a flask where the air pressure was about 25 mm. or about 5 mm. partial pressure of oxygen, and the temperature was about 200° C. Any metallic vapor will completely oxidize under these conditions if the dissociation pressure of its oxide is less than the partial pressure of the oxygen maintained in the still. This is eminently true

[1] Phys. Rev., 21, 288.

[2] L. c., p. 391.

[3] The bumping does not seem to take place with mercury when the air is all removed, as in the case of the Weinhold still, but is very troublesome when a little air is present except when it is bubbled through the mercury.

of all the common base metals. These oxides collect on the distillate and when they are present in considerable quantity as in the case of quite impure mercury, the distillate may then look dirty but when filtered through a pinhole in a filter paper is found to be free from the metals, provided sufficient air passes over with the vapors.

Mercury vapor does not seem to oxidize under the conditions given above since kilograms of pure mercury may be distilled without a suggestion of oxide appearing on the top of the "Sprengle" column (Fig. 2), while the merest trace of oxide is very noticeable. When the partial pressure of the oxygen is much more than 5 mm., mercury oxide appears. The work of Pelabon[1] indicates a very low dissociation pressure of mercury oxide at 200° C., but this is an extrapolated value and may be considerably in error. The oxides of silver, gold and the platinum metals would not form under the conditions in our still so their vapors would condense with the mercury vapor and be found as amalgams. On the other hand the vapor pressure of these metals must be very small at 200° C. as their melting points are 960° for silver, 1063° for gold and 1750° for platinum, furthermore the partial pressures of these vapors from dilute solutions in mercury would be even less than the vapor pressures of the metals themselves and it was hardly to be expected they would distill over in detectable quantities, however, it seemed well to test this conclusion experimentally.

Silver amalgams were first studied. A still, such as is described below, was charged with 6,800 grams of pure mercury and 35 grams of purest silver. It was thought that this would form a saturated solution at 200° as the solubility of silver in mercury is very small. This amalgam was distilled with a slow current of air passing through the amalgam in tiny bubbles and there was no suggestion of bumping or spurting. The fact that oxidizable metals are completely removed by one distillation in this apparatus is evidence that none of the amalgam in the still is mechanically carried over as a spray. The residue left in the still was a white sponge of silver which contained some mercury. The distillate was brought into a clean flask and distilled again, there was a small residue of silver sponge about 5 mm. in diameter left in the still together with several white spots distributed about the lower part of the still. These residues were dissolved in a little nitric acid and the solution sucked up into a little specially made pipette and then transferred to a small weighed porcelain crucible. The flask was thoroughly washed with a little water which was removed with the pipette and this washing repeated several times. The solution and washings were evaporated and

[1] C. R., 128, 825.

glowed and then heated to the melting point of silver to expel the mercury. 12.7 milligrams of silver was recovered and as this amount distilled over with 6,775 grams of mercury it appears that the distillate contained one part of silver to 533,000 parts of mercury or not quite two parts in a million when distilled from a saturated silver amalgam. This distillate had furnished a second distillate which was redistilled and a residue amounting to .19 milligrams of silver was obtained so the second distillate contained some .03 parts of silver in a million. The third distillate left no visible residue on distillation. It would therefore appear to be necessary to distill mercury at least three times if it contains silver and it is quite impossible to entirely remove silver from mercury by chemical means or any other method. It was noticed that mercury containing these small traces of silver very readily became "dirty" when agitated and was noticeably different from pure mercury in its behavior.

A gold amalgam was next distilled. 6,750 grams of mercury from the above experiment was brought into the still together with 45.5 grams of pure gold which had been electrically refined. This amalgam was distilled as above, the gold was left behind as a beautiful sponge which contained some mercury. The distillate was redistilled and left a distinct gold stain in the bottom of the still which was about 4 mm. in diameter, together with several smaller stains. These stains were dissolved in a little aqua regia, evaporated, glowed and found to weigh .18 milligrams. This gold was dissolved and determined colorimetrically by the method of T. K. Rose.[1] The color obtained was slightly less than that given by .2 mg. of gold in the same volume but the comparison was not particularly sharp. Evidently the weight obtained was reliable so the distillate from a saturated gold amalgam contains .027 part of gold to a million of mercury. The second distillate left a barely visible residue of gold which was colorimetrically determined to be very much less than .01 mg.

6,700 grams of mercury were now brought into the still together with 12.25 grams of platinum foil. This was ordinary foil which had been etched with aqua regia and then glowed. Soon after the distillation began the foil amalgamated and sank to the bottom of the still. The 12.25 grams of platinum was much more than was necessary to saturate the mercury at 200° and it was largely left behind as foil at the end of the distillation. The last of the mercury clung to the platinum foil and as it distilled the foil assumed the appearance of having been platinized. The solubility of platinum in mercury at 200° is evidently very small but the mercury was at all times saturated with platinum and must have had

[1] Chem. News, 66, 271.

a partial pressure of platinum equal to the vapor pressure of platinum at the same temperature. The distillate was redistilled and left a very distinct stain of platinum which was collected as above, evaporated glowed and again dissolved in aqua regia. It was found by a colorimetric method to be .067 mg. of platinum. If a little stannous chloride is added to an acid solution of platinum a clear golden color is obtained when the platinum concentration is very small. This color is very stable and can be quite exactly duplicated with solutions containing known amounts of platinum. It appears therefore that mercury which distills from a platinum saturated amalgam at 200°, contains one part of platinum to one hundred million parts of mercury. The 6,700 grams of mercury distilled as a vapor occupied, at 200° and 25 mm. pressure, 39,540 liters and the .067 mg. of platinum in this volume would show a partial pressure of .00000026 mm., assuming that platinum, like the other metals is monatomic in the gaseous state. This figure then represents the vapor pressure of platinum at 200°, since the amalgam in the still was saturated with platinum. This is of course only to be regarded as giving the order of magnitude of this constant, but with proper precautions there seems to be no reason why a fairly reliable value for the vapor pressures of these metals might not be obtained in this way. If we take the value for the number of atoms in a cubic centimeter of a gas at standard temperature and pressure,[1] a calculation shows that with each cubic centimeter of mercury vapor which passed out of the still there were 5.3×10^9 atoms of platinum. From this then each cubic centimeter of space or gas which is in equilibrium with platinum at 200° contains some five billion atoms of platinum.

THE PURIFICATION OF MERCURY.

Mercury is one of the indispensable things in scientific work. Some properties which render it especially useful are its density and that it is a liquid with a negligible vapor pressure while gases are insoluble in it. Mercury is acted upon chemically by but a few substances and, due to its position in the voltaic series, it may be used in contact with most salt solutions and so has played a fundamental role in the development of electrochemistry. Mercury does not oxidize readily under ordinary conditions although the dissociation pressure of mercury oxide is very small at ordinary temperatures.[2] Evidently it is a question of rate for pure mercury will remain bright in contact with air or oxygen almost indefinitely but a little ozone soon causes the mercury to tarnish, also the presence of the merest traces of metals dissolved in mercury cause it to

[1] Millikan, PHYS. REV., 32, 396.

[2] Pelabon, C. R., 128, 825.

tarnish and readily assume the form of very small globules which do not coalesce with the main mass and so the mercury acquires a "dirty appearance" and wets or sticks to glass and other substances. It is assumed that the base metal oxidizes and forms a coating about the little mercury globules but the effect may be obtained when silver, gold or platinum are dissolved in mercury. It is quite possible that the foreign metals catalyse the oxidation of the mercury. The fact is that the merest traces of foreign metals have a most remarkable effect on the physical properties of mercury and very seriously interfere with its use in scientific instruments and investigations so it is necessary to have mercury of a higher degree of purity than any other substance we work with as evidenced by the very large number of methods which have been proposed for purifying mercury.

The chemical methods depend upon the property of most metals to displace mercury from solutions. When an amalgam is brought into contact with a solution which contains mercury, the metal in the amalgam will displace mercury from the solution, but these are reversible reactions and even in the case of such electropositive metals as zinc and cadmium the removal from mercury cannot be complete and to a much less degree in the case of such metals as copper, lead and tin which are much nearer mercury in the voltaic series while there is little to be gained in the case of such metals as silver, gold and platinum by the chemical methods and acid solutions. If we treat mercury or dilute amalgams with an oxidizing acid mercury goes into solution and we have a solution containing mercury, and while some of the base metal is directly oxidized, most of it simply displaces the mercury in solution. Making mercury anode in acid or salt solutions[1] leads to the same result. In cyanide solutions mercury as anode might loose some metals more completely than in acid solutions.[2]

The well-known apparatus of L. Meyer,[3] is a most convenient and effective device for the chemical purification of mercury. The mercury flows in a thin stream through a long column of dilute nitric acid, or better a nitric acid solution of mercurous nitrate and is delivered bright and dry. This apparatus was noticeably improved by J. H. Hildebrand,[4] by a modification which allows the mercury to flow faster and still to divide into much finer globules. If an outlet tube with a glass cock is sealed into the lower part of the bend in the "goose neck" the last of the mercury and the solution may be run out separately and the appa-

[1] Jaeger., Wied. Ann. 48, 209, 1893.

[2] Battel, Chem. News, 97, 158.

[3] Zeit. anal. Chem., 2, 241.

[4] J. Amer. Chem. Soc., 31, 933 and C. I. Moore, Jour Amer. Chem. Soc., 32, 971.

ratus may be easily cleaned even when it is fastened in a permanent position. Mercury left in contact with nitric acid or mercurous nitrate solution slowly forms basic salts which are insoluble and troublesome.

The method proposed by Crafts[1] of drawing air through a long column of mercury, causes some oxidation of the base metal. It also causes a great deal of the mercury to become finely divided. We caused filtered air to bubble through a dilute cadmium amalgam (1 in 10,000) at the rate of 3 cc. per minute for four days and were able to detect cadmium in the mercury after this treatment. It is less effective than the chemical method and not as convenient.

The chemical purification of mercury is sufficient for many uses and it is a very simple and convenient operation with the V. Meyer apparatus. The chemical purification may also be effectively carried out by bringing the mercury and an acid solution of mercurous nitrate into a separatory funnel and vigorously shaking for several minutes. The mercury is then run into a second separatory funnel which contains water and from thence onto a filter with a pinhole. The chemical purification should precede the distillation so as to avoid undue clogging of the still.

The only way to effectively remove metallic impurities from mercury is by distillation and from the results given in the first part of this paper, it would seem to require two or three distillations if silver, gold or the platinum metals are present. Silver is distinctly the most difficult to remove. In the case of such metals as zinc, cadmium, lead, tin and bismuth which have a very low melting point and greater vapor pressures, it would take many distillations to satisfactorily remove these metals if the distillation was carried out in a vacuum or a reducing atmosphere. An ingenious apparatus for distilling mercury in a vacuum was devised by Weinhold[2] and modified by many other investigators. The arrangement is such that all the gases are removed by the mercury vapor and the distillation is also continuous. After the mercury vapor removes all other gases the distillation proceeds quietly and satisfactorily but we have found[3] that low melting metals like zinc distil over with the mercury and may be detected in the distillate even when there is only a trace of the metal in the mercury in the still.

We have found, however, that all oxidizable metals may be effectively removed by a single distillation if a little air is allowed to bubble through the amalgam in the still and pass over with the mercury vapor. It appears that the oxidation of the base metal occurs in the vapor phase and not to any extent while the air is bubbling through the amalgam in

[1] Bull. Soc. Chim., Paris, 49, 856.
[2] Carls, Repertorium, 9, 69.
[3] L. c., 390.

the still since the distillate from concentrated amalgams was found to be pure mercury, although the amalgam in the still contained much more base metal than could be oxidized by the small amount of air which was admitted. The following experiment was also tried: 160 c.c. of a one to ten thousand cadmium amalgam was brought into the still and was heated for four hours with air bubbling through in the usual way. The condensed mercury was allowed to flow back into the still and at the end of this time the mercury in the still had shown only a slight decrease in cadmium concentration, so it is evident that only a little of the oxygen of the air is used up in passing through the mercury in the still but in the gas phase all metallic vapors of the base metals are completely oxidized.

The question of the solubility of oxygen in mercury has been brought up by T. W. Richards and J. H. Wilson.[1] In preparing mercury for their work on amalgam concentration cells these authors used our still but employed hydrogen instead of air. This of course defeats the main advantage of this form of still. Richards and Hunt feared that the mercury distilled with air, contained dissolved oxygen but they gave no experimental evidence to support this view. The absorption of oxygen by mercury has never been detected even where the gas has been in contact with mercury at great pressures. On releasing such systems an effect should have been observed at the surface of the mercury even if the solubility was very small. Amagat[2] investigated this question and could find no evidence of absorption of oxygen at ordinary temperatures and high pressures nor any oxidation even at 100° and considerable pressures provided that the mercury and oxygen were pure. Furthermore the Weather Bureau at Washington has under observation three barometers which have been in use for over thirty years. At present they give the same readings as new barometers so there has been no deterioration of the vacuum in these barometers, and .05 mm. would have surely been detected. Now the mercury in the cisterns of these barometers soon became "saturated" with oxygen at a pressure of 150 mm. as there was contact with the atmosphere. The variations of the barometric pressure and diffusion soon brought this mercury into the barometer tube and to the top of the column where it would loose any oxygen which had been dissolved and we would expect a continually deteriorating vacuum. If the volume of the space above the mercury column is 10 c.c., .05 mm. would require only .0008 mg. of oxygen. The fact that less than this amount of oxygen got in during thirty years will give some idea of the insolubility of oxygen in mercury. The merest trace of foreign metals

[1] Zeit. Phys. Chem., 72, 136.
[2] C. R., 91, 812, and 93. 308.

in the mercury starts oxidation as evidenced by a tarnish that appears on the mercury, a most delicate test, but with really pure mercury we are of the opinion that the absorption or oxidation of oxygen by mercury does not occur or that it is an infinitesimal of a higher order.

The information gained in this and previous investigations give the essential conditions for obtaining pure mercury and it may be questioned whether any single substance may now be prepared in as high a state of purity as mercury. For small quantities of mercury a simple still may be constructed from materials found in any laboratory: Fig. 1 gives an idea of the essential details, *g* is a common "Asbestos Air Bath" with a hole in the bottom for the flame and above this there is fastened a shallow metal cup which supports the flask and on which the flame plays. The flask *a* is an ordinary round bottom flask holding from 250 to 500 c.c. The neck is drawn down short and the 20 cm. tube *b* sealed on and also the side tube *e* which is thin walled and 10 to 15 mm. in diameter and 50 cm. long, *e* serves as the air condenser. A tube *c* is selected of such a diameter that it will just nicely fit into the tube *b* and to this is sealed a glass cock while it is drawn out to a fine capillary at the lower end. This tube is slipped into the tube as indicated in the cut. The joint *d* where there is a slight enlargement of the tube *c*, is made tight with thin rubber bands which are about one centimeter wide. These bands are wrapped about the joint while stretched thus making a tight and simple joint. The asbestos shields *s*, *s* deflect the hot gases so that this joint never gets even warm to the hand. This is much simpler than a ground joint which may be used here. The glass cock regulates the rate at which the gas bubbles through the mercury in the still and if it is well ground no fat need be used on it. The end of the condensing tube *e* is sealed to the stopper of an ordinary Drexel Washing Bottle. The outlet tube from the Drexel bottle *f* is joined to an ordinary Sprengle suction pump and a manometer and a vacuum of 25 to 30 mm. maintained in the system while air is bubbling through the mercury in the still. When the still is once uniformly in operation it needs little attention and a couple of kilograms of mercury may be distilled in two or

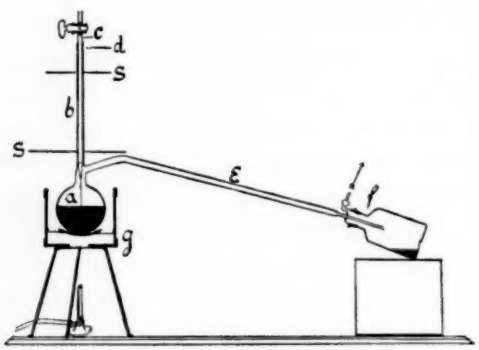


Fig. 1.

three hours. Steady gas and water pressures are desirable. It is best to avoid all organic matter, dust and fat. The ground joints may be readily made sufficiently tight by a little grinding with fine emery if they are not satisfactory to start with. The rubber joint at *d* never gives trouble if the tube fits well in the neck of the flask which is 20 or 30 cm. long.

In distilling large amounts of mercury we have found it necessary to use a larger still provided with an electric heater and arranged to permit of introducing mercury into the still during the distillation. The main features of the still we are using are represented by the sketch in Fig. 2. The flask *a* is about 15 cm. in diameter and into the bottom is sealed the glass tube *e* which connects with the reservoir *h*. The cock *g* is ordinarily open but is often found to be necessary. It was found that the air might be admitted from below through the side tube *s* instead of from above through the neck as in the proceeding still. *f* is a ground glass joint, the tube ends in a capillary which delivers the air well into the tube *e* where it bubbles up through the mercury and into the still. With this arrangement one can always observe the rate at which the air is passing into the mercury and control it with the cock *i*. Mercury is allowed to flow into the reservoir *h* at any desired rate and this controls the rate at which the mercury enters the flask *a*. The mercury vapor is condensed in the large "U" tube *c*, *c* which is made from 25 mm. thin-walled tubing and is 50 cm. long, thus giving a condensing tube one meter long. The tube *o* is joined to a Sprengle suction pump and manometer and a vacuum of 20 to 30 mm. maintained in the apparatus during distillation. The mercury condenses in the tube *c*, *c* and collects in the tube *d* and flows out at the bent up end. This tube *d* is about a meter long and 4 mm. in diameter.

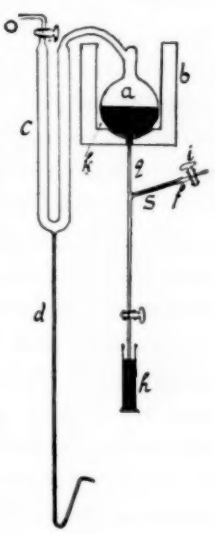


Fig. 2.

b, *b* is an electric heater made from asbestos, water glass and magnesium oxide cement. The heating coils are of "nichrome" ribbon and are located on the sides and bottom. The bottom part of the still is made from strips of asbestos 40 mm. wide and 1.5 mm. thick. The nichrome ribbon is placed along the edge of these strips and then they are rolled up together forming the ribbon into a spiral very close to one side of the "wheel" formed. The asbestos strips are well wetted with water and the waterglass-magnesium oxide mixture and after it is wound it may, while still wet, be dished to fit the form of the bottom of the flask. This

gives a good support to the flask and the heating coil is right where it will be most effective. A short piece of brass tubing is attached to the end of the nichrome ribbon as a convenience in starting the roll. This brass tube serves as a hole for the tube *e* and also as one terminal for this heating coil. For 110-volt circuits this coil should have a resistance from 12 to 15 ohms.

A thin piece of asbestos is wound on a cylindrical form of the desired diameter. The asbestos "wheel" just made is forced into one end of the cylinder and on the outside is wound nichrome ribbon to form the heater for the sides, about 5 or 6 ohms are needed here. About the cylinder is wound a layer of asbestos wet with the cement and over all several layers of asbestos for insulation. The top of the heater is also covered with asbestos and glass wool. Some more resistance will be needed if all the heat from the 110-volt circuit is to be used in the heater. This is easily accomplished by making a spiral of nichrome wire and placing it in the lower inside corner of the heater *k*, *k*. The resistance of this coil may be adjusted so that no external resistance need be used and when working normally the rate of distillation should be such that the mercury vapor is condensing over nearly the whole length of the condenser. Our still takes 4.6 amperes at 110 volts and distills about two kilograms an hour. The electrical energy used is thus about half a kilowatt hour for two kilograms of mercury and at the high rate of 10 cents per kilowatt hour this would cost only 2½ cents a kilo for the electrical energy. If the heat needed to evaporate a kilo of mercury is 62,000 calories it would seem that only about one third of the heat generated by the current was used in volatilizing mercury. The still needs little attention when once in operation and will easily distill 20 kilos a day.

This apparatus is fastened to an upright support which is part of a large tray, a bracket holds the heater. After using the still the last of the mercury is run out and acids drawn up into the flask *a* and the condensing tube if necessary. One to one nitric acid is best for this purpose and is followed with distilled water. The still is easily cleaned and dried without dismantling. The glass cocks should be well ground so as to avoid the use of fat or organic matter, the cocks need not be perfectly tight. In constructing and assembling this apparatus a hand blowpipe was found to be indispensable.

PRINCETON, N. J.,
July, 1911.

THE EXCEPTION TO HOOKE'S LAW.

By Julian C. Smallwood.

THE phenomenon which it is the purpose of this article to describe was first observed by the writer during an investigation (still in progress) of the drum motion of a steam engine indicator. This motion is not exactly proportional to that of the steam engine cross-head because of the stretch of the cord transmitting it. The stretch, of course, depends upon the stress existing in the cord, and as the stress varies from point to point of the motion cycle, there are errors in the indications of the instrument. In the primary investigation, the problem was attacked by first obtaining autographic diagrams of the cord stress. The cord was then tested for the relation between stress and strain under static conditions. This test was made by *adding* dead weights and measuring corresponding elongations, but no measurements were made under decreasing loads. The result was a confirmation of Hooke's law. Other experiments, however, indicated that this law did not obtain. It occurred to the writer that perhaps a different law governed the relation between stress and strain when the stress was rapidly varied. So an experiment was devised by which an autographic stress-strain diagram could be secured under the condition of rapid motion.

The apparatus is shown by Fig. 1. It consists of a reciprocating cross-head, *C*, carrying a bell-crank lever, *L*, to the short arm of which is attached a spring by means of a spindle, *S*, the spring being mounted on the cross-head. The other arm carries a pencil point which traces the diagram upon a stationary slip of paper, *P*. In operation, a long cord, *K*, is attached to the spindle at one end, the other being tiedto a stationary point. As the cross-head reciprocates, the string is stretched in amounts nearly equal to the horizontal motion of the pencil. The stress in the cord is transmitted to the spring which elongates or contracts accordingly, such elongation or contraction giving a corresponding vertical motion to the pencil point. This motion is roughly proportional to the stress causing it. The cross-head being reciprocated, there results a stress-strain diagram under the

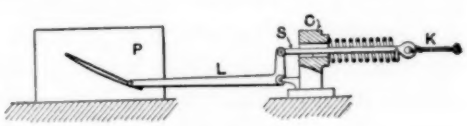


Fig. 1.

desired conditions, which may be corrected vertically for the kinematic error of the bell-crank and horizontally for the stretch of the spring.

Fig. 2 is such a diagram, corrected, and reveals an unexpected result. As the stress increases, the stretch varies directly with it, but, in decreasing, this relation no longer holds. The curve representing the decreasing values approximates to a circle. The cord does not return to lengths corresponding to the previous stresses except at the initial load. Upon being stressed again with first increasing and then decreasing force the identical variation is repeated.

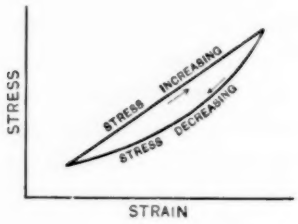


Fig. 2.

Fig. 3.

Fig. 3 is a copy of an actual record which was taken in order to determine if the relation between stress and strain was at all dependent upon the speed of application of the stress. The oscillation of the cross-head was first made very slowly (about 10 seconds in duration) and a diagram recorded. The speed was then increased to about 100 oscillations a minute and another diagram recorded on the same paper. This procedure was repeated, the speed being varied up and down for five minutes from very slow to 600 oscillations a minute, and occasional diagrams taken. No matter what the speed, the pencil traversed the same curve with remarkable precision, whatever blurring of the lines that occurred being due to the violent swaying of the cord at the high speeds. The curvature of the upper line of Fig. 3 is due to the kinematic error of the bell crank, previously mentioned. When this is allowed for, the ascending curve becomes straight.

The original record is a combined stress-strain diagram of the cord and spring. The stretch of the spring, however, was small compared with that of the cord, so its influence to alter the relation sought was probably slight. But, to be sure that the inertia or the friction of the link work of the recording mechanism did not cause a false record, a static test was made in this manner. Fifteen feet of previously stressed cord was hung and a scale poise tied to its lower end. One pound weights were placed successively upon this poise and the corresponding cord

elongations measured, the time intervals between the additions of weight being constant, fifteen seconds. The weights were then removed in the same way and the elongations under decreasing loads recorded. When the results were plotted, the same character of curve appeared as in the motion tests, and showed practically the same relation quantitatively.

By another device, similar in principle to Fig. 1, were obtained superposed diagrams for various ranges of stress. Fig. 4 is such a one, cor-

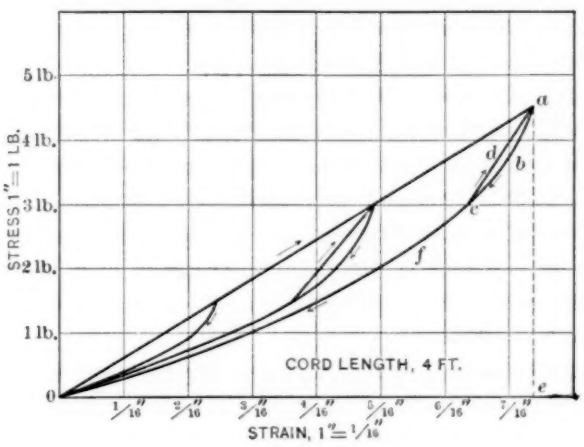


Fig. 4.

rected. Upon increasing the stress from zero to four and one half pounds, decreasing to three, and then increasing again to four and one half pounds, the curve traversed is 0*abcda*. Similarly for the other ranges of stress. It is seen that the higher the stresses limiting a given range the less is the stretch produced in that range, that the ascending curves are all straight lines although of different slopes; and that the descending curves are arcs.

The following explanation of the departure from Hooke's law is so obvious that it seems remarkable it was not foreseen. In Fig. 4, the area 0*ae* is a work diagram, being the product of force and distance. This area represents the work done on the cord. Now, when the force is decreasing, the cord shortens because of the tension of its fibers, and therefore performs work. This is represented by the area 0*fae*. If the stress curve returned upon the same line as that upon which it advanced, the one area would equal the other; that is, the work delivered by the cord would be equal to that done upon it. This would be equivalent to the operation of a perfect machine, one having one hundred per cent. efficiency, which is impossible. The area 0*af*0 measures the lost work caused by the friction of the fibers of the material.

This physical property, it will be noted, resembles the magnetic one known as hysteresis. As the physical property is due to the reluctance of the fibers to return to their original shape, the term "lag" is perhaps an appropriate name for it.

There is nothing to indicate that the reasoning just given applies only to a woven fabric like indicator cord. Although the phenomenon of lag has a decided bearing upon the records of a steam engine indicator, its chief importance may lie in its occurrence in other materials. In view of the fact of molecular friction which is exerted when any material changes shape, this property *must* be a characteristic of *all* materials. If Hooke's law obtains with increasing stress, it cannot do so when the stress decreases. Following this conclusion, many interesting conjectures may be made regarding the result of lag upon the records of instruments of precision, especially those dependent upon springs. Theoretically. such instruments, if indicating correctly upon an increasing scale, cannot do so when the measured quantity decreases. The question at once suggests itself, is the departure of the two scales sufficiently marked to receive serious attention?

The writer has made some experiments upon springs with the purpose of answering this question. The results, however, were not sufficiently reliable to quote, the apparatus being crude, but it may be said that the up and down curves did not appear to vary materially.

On the other hand, the writer has tested a transmission power dynamometer (depending upon the twist of a spring for its indications) and discovered a difference of about two per cent. at the maximum between the up and down scales. It should be noted however, that this difference must have been due not only to the internal friction of the spring but, in part, to that of a roller bearing which supported the shaft delivering the power.

It is recognized that, in the calibration of an indicator spring, it is necessary to obtain two scales, one for ascending, the other for descending pressures. The differences between these scales have generally been attributed to the friction of the indicator piston in its cylinder and of the joints of the pencil motion. It is possible that they are also due to the molecular friction of the spring.

An occurrence was related to me by an eminent engineer which illustrates in an interesting way the effect of lag upon an instrument of precision. This gentleman had several very sensitive aneroid barometers which he wished to test. Having occasion to take a railroad journey which necessitated crossing a mountain, he took along his barometers, and, as the ascent, was made, compared their indications. These coin-

cided very closely. But, upon descending, he found them very much at variance. The barometers were quite differently constructed, especially as to moving parts, so he concluded that it was the internal friction, being different in amount in the different instruments, which caused their lack of harmony. In his own words, " Those that had the greatest friction needed more *time* to come back." But, as the writer has pointed out, the phenomenon of lag, at least as manifested by cord, is independent of the element of time.

Another interesting result of lag is the consequent variation in the coefficient of elasticity. Instead of being a constant, this quantity depends upon the range of stress as shown by Fig. 4. Whether or not its variation is material, in the case of metals, is open to investigation.

Further, the question of the *efficiency* of materials may be worthy of investigation. It appears that the true measure of the resilience of a material is the product of the work done upon it and its efficiency, this product being equal to the work returned by the material as its fibers resume their original shape. Is this efficiency constant or does it vary with the range of stress?

It may be that the phenomenon of lag has more claim upon academic than practical interest, and that its effect upon precision measurements, as far as molecular friction is concerned, is trifling. At all events, it seems worth while to investigate further whether or not this is the case.

A SIMPLE PROOF OF POYNTING'S THEOREM.

BY J. F. H. DOUGLAS.

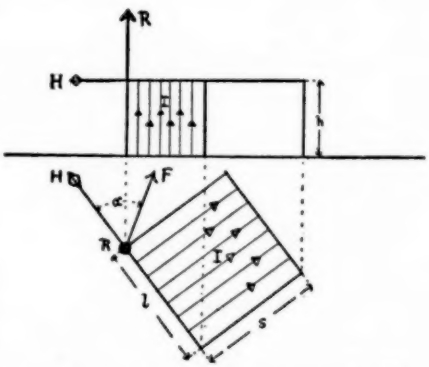
POYNTING'S theorem, which states the law which electrical energy observes in its flow through space, offers some difficulties to a beginner. In the case of a direct-current circuit everything in space outside of the wire seems to be static, and power without motion is hard to conceive. Moreover, the mathematical proof usually given is not simple enough to suggest any mechanism by which the power flow can take place. The result also is uncertain by a function which would integrate to zero over the boundary of the region considered.

If power is actually flowing through space, so that it enters some sides of a box cut out of space and leaves others, the fact is obscured by the apparent absence of any action of the particles inside the box upon the particles outside the same. If, however, we could isolate an element by any means from its neighbors, the power flow should be apparent at the boundaries. Thus where power was entering the element there should be a source of energy, and where the power was leaving the element there should be a consumption of energy.

The magnetic field within any tube of magnetic force may be considered as due to a current circulating around it. This current will have the same number of ampere-turns as the current in the conductor which produces the field. Such a combination is equivalent to the original one; for, if combined, the currents would all cancel each other outside the conductors. Moreover, if the currents are distributed in proportion to the intensity of the field, each current would produce no action outside the tube it surrounds. Thus the current wrapping for a given element would be adequate to produce the magnetic field within it. The element being shielded from magnetic forces, the only work done at the boundaries must be electrical work. Therefore, this must be done by virtue of the electric field. The current, which we suppose to circulate around each tube of force, in some places flows against and in some places with the electric field. Hence, in some places energy is leaving the electric circuit for the interior of the element; and on the opposite side, while flowing in the same direction, leaves the element for the electric circuit. Thus, the desired isolation is secured, and the action at the same time is seen to be a dynamic and not a static one.

Poynting's theorem states that energy flows in a direction perpendicular to both the electric and the magnetic fields. It is natural, therefore, to take as our element a portion of a tube of magnetic force bounded by surfaces in the plane of the magnetic and electric fields, and by surfaces perpendicular to this. Referring to the sketch we shall see, that in order to produce an internal magnetic field of H ampere-turns per centimeter, we need a current around the box of

$$I = H \times l \text{ amperes.} \qquad (1)$$



An Element of the Electromagnetic Field Showing the Flow of Power.

This current flows at right angles to the electric field on the two sides of the box and hence does no work there. It flows with the electric field on the top of the box and against it on the bottom of the box. Electrical energy is being consumed on the lower or "motor" side to supply the energy which flows upward. This energy reappears as electrical energy on the top or "generator" side. The work done on either face is EI watts where E is the voltage drop across the face of the element. But

$$E = F \times s \times \text{Sin } \alpha \text{ volts,} \qquad (2)$$

where F is the number of volts per centimeter. Hence the power

$$W = E \times I = F \times H \times (\text{Sin } \alpha) \times s \times l \text{ watts,} \qquad (3)$$

and the power flow per square centimeter is

$$R = W/(s \times l) = F \times H \times \text{Sin } \alpha \text{ Watts per sq. cm.} \qquad (4)$$

This is Poynting's theorem. Although the proof is given in the practical units, it would have been just as easy to use the C.G.S. units instead.

The similarity of magnetic circuit relations to those of the electric circuit permit us to speak of magnetic "current" and magnetic power.[1] We could, therefore, have isolated our elements by wrapping the tubes of electric force with magnetic currents. The proof in this case would have been just as direct. However the assumption of electric currents was chosen as the more natural.

It could be proved, along lines similar to those above, that the energy flow given by equation (4) will account exactly for the increase or decrease

[1] See Oliver Heaviside, *Electromagnetic Theory* (1893), Vol. I, p. 25.

in the energy within any volume. There would be no point in doing so for two reasons. First, although perhaps somewhat shorter than most proofs, it would really be the same as that usually given as a proof of Poynting's theorem.[1] Second, such a proof would seem unnecessary when once we concede that the energy does flow according to the above law (Eq. 4).

The generality of the proof given here deserves some further consideration. Since the method used does not depend upon a surface integration, there is not that uncertainty in the proof, which always goes with the attempt to find the integrand which gives a certain integral. Moreover, the mathematics are so simple, that chance for ambiguity in other directions is hard to see. Thus any limitations as to the definiteness of the result should lie in the physical conceptions here presented and not in the mathematics. The writer believes that the assumptions are at least natural, and that the proof helps to make the rationale of the process of energy flow plain.

[1] For example see that in Dr. J. G. Coffin's *Vector Analysis*, pp. 164–165.